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A Study of the Solubilization of Compounds of the Types Found in the Resinous Fraction of Wood Pulps

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A STUDY OF THE SOLUBILIZATION OF COMPOUNDS OF THE TYPES FOUND IN THE RESINOUS FRACTION OF WOOD PULPS

A thesis submitted by

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TABLE OF CONTENTS

INTRODUCTION

Pitch formation and self-sizing (or loss of absorbency) are two problems encountered by papermakers which are attributed to the resinous constituents of wood pulps prepared by the nonalkaline processes. The presence of small quantities of residual resin in dissolving-grade pulps is thought to lead to weakened rayon filaments and also to be a factor contributing to spinneret cratering in the regeneration step of the rayon process.

With the increased activity in the high-yield pulping field the problems associated with the resin fraction of these pulps will become more prevalent and effective means of reducing the resinous material will be required.

At least three methods of reducing the resin content of certain pulps are worthy of consideration. Since the resinous components are largely contained within small parenchyma cells of the wood, a mechanical separation of this fraction of the pulp has been advanced as a means of alleviating resin-derived problems. Fractionation (1) has been utilized with success, but leads to relatively high losses of yield and requires large quantities of water.

The resins conceivably could be extracted with organic solvents, but the high costs of these solvents and the accessories necessary to effect solvent recovery tend to place this plan on what might be termed a "last resort" basis.

The possibility of reducing the resin content of pulps through some undefined detergent mechanism has been considered for several years.

G. A. Richter (2), in 1941, reported that detergents (in this case, sulphated fatty alcohols and soaps) could be added to the alkaline extraction stage of the bleaching operation to obtain pulps containing less ether-soluble material than could be obtained using an alkaline treatment alone. Nihlen (3) conducted similar experiments. Hoos (4) patented a high temperature sodium oleate-caustic process for removing resinous materials from dissolving grade pulps. Back (5) found that tall oil soaps could also be utilized in effecting resin removal. In the early 1950's, the nonionic detergents appearing on the market were investigated and found to be very effective deresinating agents. Rapson (6) in Canada and Samuelson (7) in Sweden obtained patents on the use of certain nonionic surface-active agents as deresinating agents to be used in conjunction with the alkaline treatment in the bleaching process.

The effectiveness of the nonionic detergents as deresinating agents should serve to stimulate interest in this means of removing the resinous materials. In the development of new and still more effective agents some knowledge of the mechanism whereby the added detergent aids resin removal would seemingly be highly desirable. Logically, the properties exhibited by relatively dilute detergent solutions should be examined as a first step. Back (5), following this line of thought, theorized that the solubilization phenomenon was involved. Further study indicates that this phenomenon might well be active in deresination and worthy of consideration.

Solubilization is the name given by McBain (8) to a particular mode of bringing into solution substances that are otherwise insoluble in a given

medium. Solubilization involves the previous presence of a colloidal solution whose particles take up or incorporate within or upon themselves the otherwise insoluble material.

The importance of this means of dispersing the water insoluble resinous materials of the types present in pulps cannot be determined from existing information. The study to be presented was undertaken, at least in part, to gain this information. In addition, certain information regarding the nature of the solubilization process was also sought.

GLOSSARY

Association Colloid. A colloid formed by the reversible association of amicroscopic molecules. Molecules which associate to form this class of colloids commonly possess a large dipole moment and are strongly anisodimensional. Salts of the higher fatty acids, the soaps, are typical association colloids. Aggregates of an association colloid are commonly termed "micelles".

Colloidal Electrolyte. An association colloid formed by an electrolyte, the aggregate being colloidal but possessing many of the properties of ordinary electrolytes.

Deresination. See Deresinification.

Deresinification. A term used in patent literature to describe the operation of removing the resinous material from a pulp or other resin-containing material. Swedish patents used the term "deresination" to describe the same operation.

Micelle. See Association Colloid.

Polyethenoxy Alkyl Ether. The product formed when ethylene oxide is reacted with an aliphatic alcohol, commonly a fatty alcohol, according to:

$$CH_3(CH_2)_xCH_2OH + n\underset{\diagdown O \diagup}{CH_2CH_2} \longrightarrow CH_3(CH_2)_xCH_2OC_2H_4(-OC_2H_4)_{n-1}OH$$

Solubilizate. The water-insoluble material which goes into "solution" in the presence of an association colloid. The solubilizate in the

solubilization phenomenon might be considered to be roughly equivalent to the solute in the ordinary dissolution process.

Solubilization. Aqueous solutions of association colloids possess the property of being able to bring into solution, in a thermodynamically reversible manner, appreciable quantities of compounds generally considered to be water insoluble. J. W. McBain (8) termed this process "solubilization". McBain originally defined solubilization as "a particular mode of bringing into solution substances that are otherwise insoluble in a given medium. Solubilization involves the previous presence of a colloidal solution whose particles take up and incorporate within or upon themselves the otherwise insoluble material."

Solubilizing Agent. The water-soluble compound responsible for solubilization. Aggregates of these compounds are formed in dilute aqueous solutions, i.e., these compounds exhibit a marked tendency to associate at low concentrations. Actually, the aggregates of the given compound effect solubilization. Most of the more common solubilizing agents might be loosely considered to be detergents.

Solvation. The term used to denote the total interaction between an ion or molecule and a solvent. In this work, hydration and solvation will be used interchangeably.

Resinous Fraction (or Compounds). The fraction of the wood and/or pulp which is extractable with organic solvents such as ether, acetone,

or alcohol and is composed of resin and fatty acids, esters of these acids, and unsaponifiable material consisting of sterols, alcohols, waxes and resenes.

BACKGROUND DEVELOPMENT

The conventional textbook treatments accorded the subject of solubilization all seem slightly inadequate in that the phenomenon is not related to the over-all behavior of the three-component systems involved. To place solubilization in the proper perspective, ternary equilibrium diagrams for systems exhibiting this property should be examined.

A schematic isotherm for the system potassium laurate-lauric acid-water, reported by McBain and Field (9), may be assumed reasonably typical and used for illustrative purposes. The homogeneous region to the right in Figure 1 is the region of solubilization. If, for example, lauric acid is added to an aqueous potassium laurate solution of concentration C (following path CA), the system will remain homogeneous until the heavily-shaded boundary is reached. At this boundary, the aqueous laurate solution is saturated with lauric acid and further additions will cause a second phase to appear, the compositions in equilibrium being determined by the tie-lines. Actually, most of these three-component systems are relatively complex, with one or more anisotropic phases appearing at high concentrations of the soap (10-12).

The particular system presented in Figure 1 has been studied up to 350°C. At elevated temperatures the two isotropic regions merge, the three components becoming completely miscible except at very low and very high concentrations of soap. Phase diagrams for other systems have been determined (10-12), but few have been as extensively investigated as the one discussed.

In the usual series of solubilization experiments, the data obtained

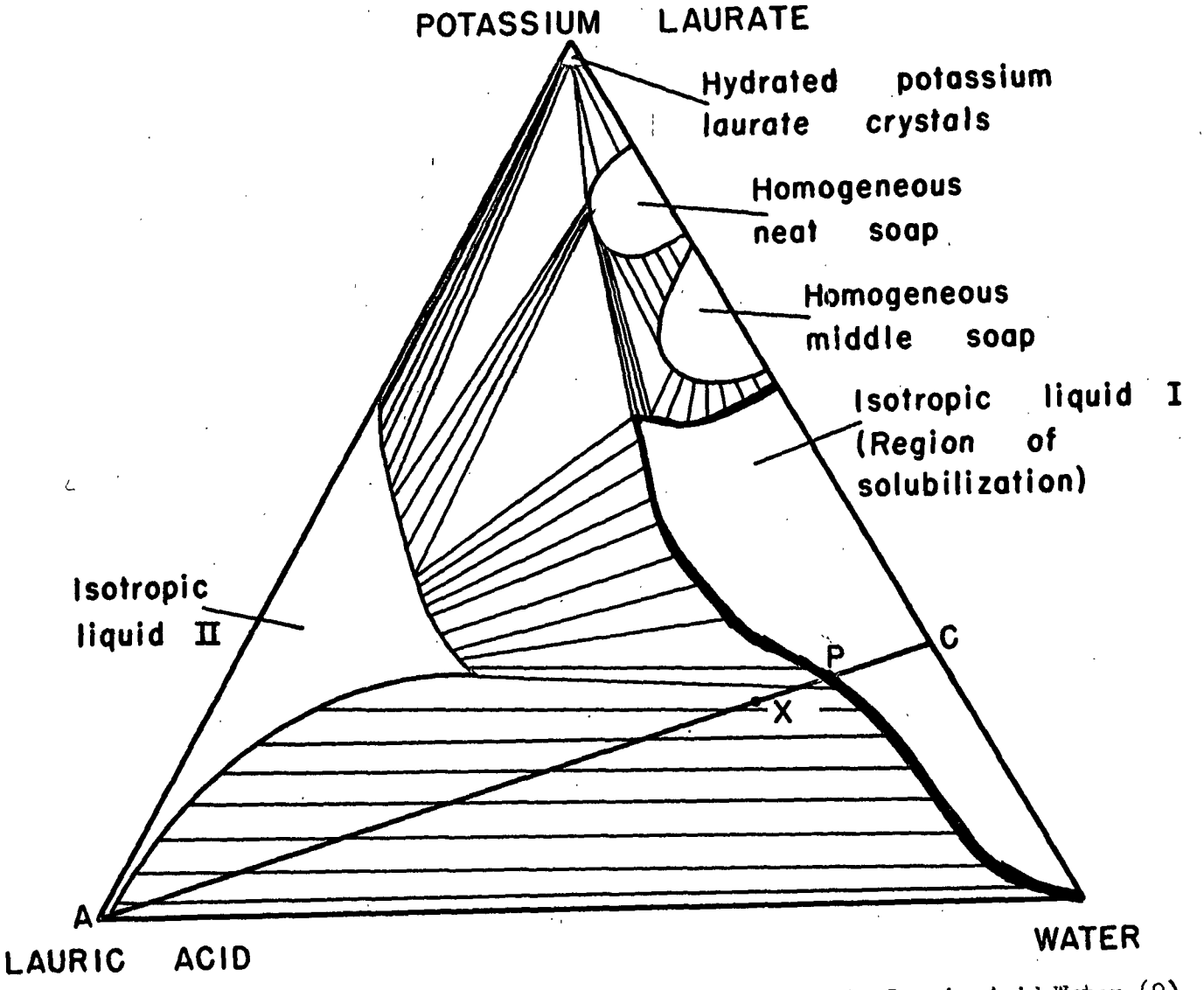


Figure 1. Schematic Isotherm for the System Potassium Laurate-Lauric Acid-Water (9).

enable only the heavily shaded phase boundary (limit) to be located. More often than not, the nature of the phase appearing when this limit is exceeded is not determined. In some systems, particularly at low soap concentrations, excess nonpolar solubilizates are reported to appear free in an emulsified state. When polar solubilizates are added in excess (of the limit), a phase composed of all three components appears (not emulsified solubilizate).

The equilibrium diagram does not give any information regarding the mechanism whereby dilute solutions of soaps and other detergents are able to render ordinarily water-insoluble materials apparently "soluble". To explain this unusual behavior, both the bulk and surface properties of aqueous solution of these compounds have been studied. In very dilute solutions, these materials behave ideally. At somewhat higher concentrations, but still dilute, marked deviations from ideality are observed. Plots of surface tension versus concentration (13, 14) yield curves convex toward the origin (Figure 2). The surface tension decreases very sharply initially, breaks, and then continues to drop slowly as the concentration is increased. Plots of equivalent or molar conductance against concentration (15) exhibit similar properties (Figure 3). At very low concentrations, the conductance drops gradually as the concentration is increased. This normal or ideal behavior is rather sharply interrupted, a marked deviation from ideality being observed. Similar deviations are noted for the osmotic, diffusion, optical, and other electrical properties (16). Nonionic compounds which are capable of effecting solubilization exhibit the same types of deviation as the ionics from ideality in surface (17) and optical properties (18).

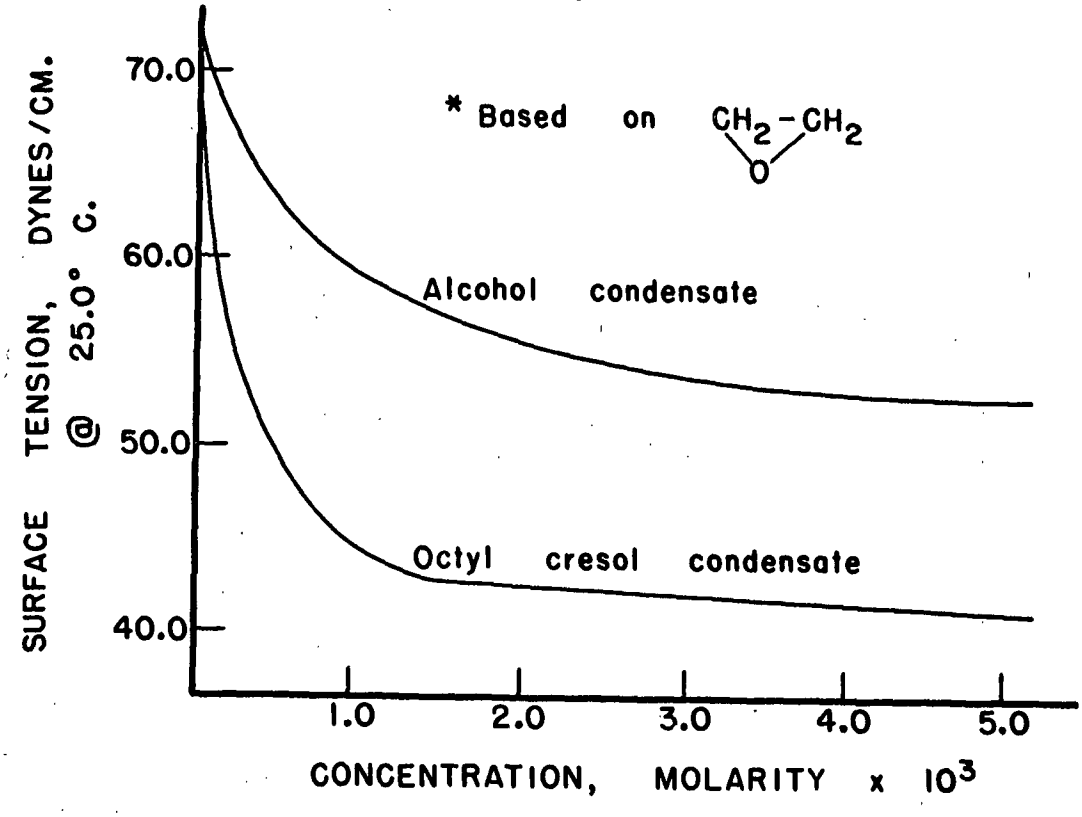


Figure 2. Surface Tension-Concentration Relationship for Two Nonionic* Surface Active Agents (50)

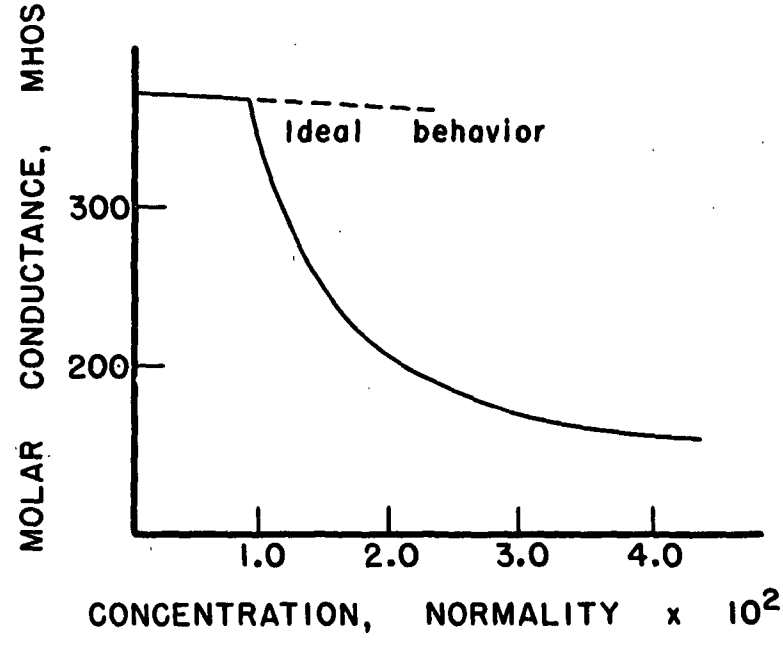


Figure 3. Molar Conductance-Concentration Relationship for an Ionic Surface Active Agent (23)

The changes which are observed in the gross properties of these systems over the transition region are attributed to the onset of appreciable aggregation of the dispersed material, the deviations from ideality being best interpreted as being due to such an association. Since only those solutions of concentration greater than that concentration at which the transition occurs are capable of solubilization (12), the logical conclusion is drawn that the solubilized material becomes associated in some manner with the aggregates or micelles of the dispersed compound.

While it is generally accepted as fact that aggregation takes place, much conjecture concerning the nature of the association exists, i.e., the size and shape of the aggregates formed. Hartley (19) suggested that the aggregates or micelles of ionic compounds were essentially spherical in shape and possessed a variable charge, the charge being a function of the concentration. Debye (20) proposed a sausage-shaped model. McBain (21) held that a single partially charged micelle could not explain all properties exhibited by aqueous solutions of these materials and considered a second type of micelle, a lamellar aggregate, to be also present in solution. This latter type of micelle was considered present in concentrated solutions. Some support for this concept is gained from x-ray diffraction studies (22). Solutions of colloidal electrolytes in the 5-20% concentration range yield diffraction patterns which are interpreted as supporting the lamellar structure. In many cases, the information derived from the x-ray diagrams has been satisfactorily correlated with the dimensions of the molecules being studied. Light scattering techniques (23) have been utilized as tools for determining the size of micelles present in solution. These data cannot

be interpreted directly because of the absence of specific information regarding the shape and size distribution of the aggregates.

Several theories have been presented to account for the formation of micelles in aqueous solutions of colloidal electrolytes. According to these treatments, micelles are formed because the hydrocarbon tails of these molecules possess a lower energy in the aggregated state than when surrounded by water molecules. Debye (24) first attempted to treat micelle formation in a quantitative manner, seeking to explain the reasons why micelles do not grow indefinitely. In this theory, two factors were considered: the van der Waals attractive forces between hydrocarbon chains and the electrostatic repulsive forces between the charged heads of the molecules. The total work involved in assembling a disk-shaped micelle was theorized to be:

$$\underline{W} = \underline{N}^{\frac{3}{2}}\underline{W}_E - \underline{N}\underline{W}_M, \text{ where}$$

$\underline{N}$ is the number of ions involved, $\underline{W}_E$ is a constant related to the attractive energy between hydrocarbon chains, and $\underline{W}_M$ is a constant related to the electrostatic energy associated with the charged ionic heads. When $\underline{W}$ is plotted against $\underline{N}$, a curve exhibiting a minimum is obtained. The value of $\underline{N}$ obtained at this minimum was assumed by Debye to represent the preferred or stable size for the micelle.

Reich (26) presented an analysis intended to apply to associating nonionic compounds. Aggregation was considered to proceed until as much of the hydrocarbon-water interface as possible was eliminated. For a pure hydrocarbon the whole of the interface could be eliminated, i.e., aggregation

could proceed indefinitely, corresponding to phase separation. Aggregates of infinite size were not considered likely, for energetic reasons, for detergent molecules possessing polar groups. The conclusion was drawn that the micelles of these compounds must be spherical in shape, the hydrocarbon tails fused into what might be considered a tiny hydrocarbon droplet with the polar tails emerging, tentacle-like, from the surface of the droplet. According to this treatment, the aggregate must be spherical in shape if the maximum hydrocarbon-water interface is to be eliminated. On the basis of rough estimates of the enthalpy and entropy changes involved in the aggregation process, a size distribution function for the micelles in solution was derived.

Ooshika (25) presented a modified theory of micelle formation, which was, essentially thermodynamic and involved the minimization of a function assumed to represent the free energy of the system. The function presented in this paper possessed a minimum and hence a preferred micellar size could be shown to exist.

With the development of statistical theories of linear polymer solutions (27), attempts were made to adapt these theories to solutions of associating solutes.

In utilizing these concepts, the assumption is made that the given substance is capable of associating by the reactions:

$$A + A \rightleftharpoons A_2 \qquad (K_1 = \text{equilibrium constant})$$
$$A_2 + A \rightleftharpoons A_3 \qquad (K_2)$$
$$A_3 + A \rightleftharpoons A_4 \qquad (K_3)$$
$$\vdots$$
$$A_n + A \rightleftharpoons A_{n+1} \qquad (K_n)$$

and that the equilibrium constant for each step is the same, i.e., $K_1 = K_2 = K_3 = K_n$. Assuming the associating effect in solution is directly related to the volume fraction of the associating component (28), it becomes possible to calculate a size distribution curve for the associating component in solution. Meyer and van der Wyk (29) were the first to indicate that such a technique might apply to solutions of association colloids. These workers pointed out that the assumption inherent in this type of calculation is that the free energy change per molecule entering an aggregate is independent of the size of the existing aggregate, i.e., this free energy change is assumed constant. When this approach is applied, no preferred or stable aggregate size is seen to exist. Rather, a most probable distribution results, the nature of this distribution being dependent upon the value of K and the concentration of the associating compound. Using a function of this type, no sharply defined critical concentration for micelle formation can be determined. This does not, however, seem to be a serious objection, since the experimentally determined critical concentration can be redefined, e.g., in terms of the attainment of a mean size for the aggregates. Such a distribution might be expected to apply to nonionic materials. With colloidal electrolytes, the equilibrium established between aggregates and the unaggregated material is less simple, i.e., the gegenions are involved. This type of treatment would apply only if the ratio of cations to anions in the aggregate were fixed. This latter assumption appears to be a good first approximation and the possibility of applying the mentioned distribution function to ionic detergents, at least in dilute solution, cannot be dismissed.

Vold (30) used a mass law approach in attempting to determine whether or not a single preferred aggregate or a broad distribution of aggregates occurred in solution. Osmotic pressure data were used in an attempt to verify the derived expression, but the results were inconclusive.

Although the character of the aggregation must be a significant factor influencing the extent of the measured solubilization, certain empirical aspects of the solubilization process can be discussed further in a qualitative manner acknowledging only that aggregation is a prerequisite to solubilization. In order to establish some basis for discussion, the views of Hutchinson and Harkins regarding the manner in which solubilization takes place and the relationship between the solubilizate and the aggregated solubilizing agent will be considered.

Hutchinson (31) considers the aggregation process as the formation of a pseudo-phase. A spherical model is assumed for the aggregate, the interior being assumed to possess the same properties as the parent hydrocarbon and the polar heads oriented toward the aqueous phase. The solubilization process can then be considered as a distribution phenomenon, the solubilizate being partitioned between the aqueous phase and the "micellar phase". This treatment assumes all solubilizable materials are slightly water-soluble. In general, the solubility of the solubilizate in the micelle is assumed to be about the same as in the bulk hydrocarbon to which the hydrocarbon portion of the solubilizing agent molecule is related.

Harkins (32) postulated that the solubilizate could become associated with the micelle in one of three ways. In the solubilization of nonpolar

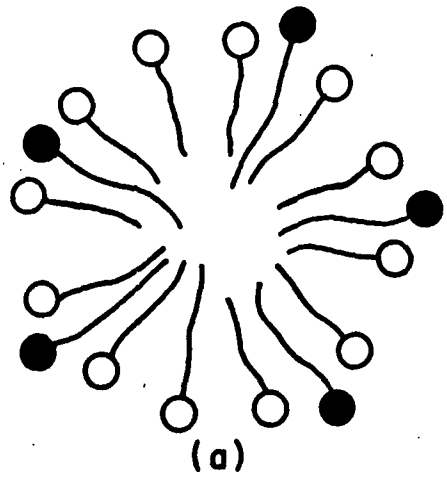
compounds, e.g., benzene and toluene, the solute molecules are not oriented with respect to the aqueous phase (Figure 4b), but are almost completely associated with the hydrocarbon interior of the aggregate. In the solubilization of a polar compound, e.g., a fatty acid, the polar end of the molecule is assumed oriented toward the aqueous phase, i.e., these compounds penetrate between the molecules of the solubilizing agent of the aggregate (Figure 4a). Finally, the assumption was made that certain sparingly soluble dyestuffs could be adsorbed on the micelle surface.

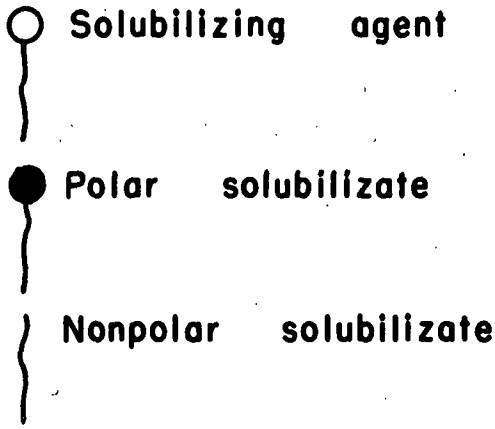
Various means of determining the capacity of a given solution to solubilize a water-insoluble material have been utilized. Considering the phase diagram (Figure 1), the addition of solubilizate beyond the limit will result in the appearance of a second phase. The nature of this second phase depends on the system being studied, but in any case, the two-phase system gives rise to a turbidity (33) which can be measured by optical means, the onset of the turbidity indicating the appearance of the second phase. This is by far the most widely used method. Other means of detecting the solubilization (12) limit depend on changes in conductivity, viscosity, and density as the system becomes heterogeneous.

The extent to which a given compound is solubilized is apparently a function of the concentration of the particular agent used. If the mole per mole ratio (i.e., moles solubilized per mole of solubilizing agent) is plotted as a function of concentration (33), the curve shows an initial sharp rise and then tends to level, the rise being very gradual. If the moles solubilized per unit volume of solubilizing agent is plotted versus

(a) Solubilizate oriented with respect to solubilizing agent

(b) Nonpolar solubilizate to the interior of the aggregate, not highly oriented





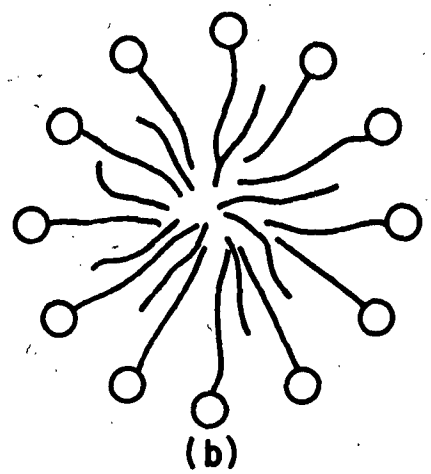


Figure 4. Schematic Representations of the Locations of Solubilized Compounds in Spherical Micelles [According to Harkins (32)]

concentration, the resulting curve is almost linear, although more frequently it is slightly concave toward the ordinate. All the more common data were obtained over the 25-40°C. range.

For a given solubilizate, the longer the hydrocarbon portion of the solubilizing agent molecule, the greater the solubilization, for a given end group (34). No definite conclusions can be drawn regarding the effect of the hydrophilic or polar group of the solubilizing agent molecule (at fixed chain length) on the extent of the measured solubilization although some inconclusive data have been presented (35).

McBain and Richards (36) have conducted a series of experiments in which an attempt was made to correlate certain properties of various solubilizates with the extent to which these compounds could be solutilized at a fixed temperature and fixed concentration of the solubilizing agent. The study was inconclusive, but for certain hydrocarbons the extent of solutilization was found to be inversely proportional to the molar volume of the solubilizate.

The addition of simple electrolytes to the aqueous solubilizing agent solution has been observed to markedly influence the extent of the measured solubilization. Although a relatively large body of data have been reported, the results in many cases are contradictory. Klevens (37) has presented data showing that the gegenion of the micelle increased the solubilization of nonpolar hydrocarbons, whereas the solubilization of polar solubilizates was depressed by the added gegenion. Ions of the same charge as the micelle have also been observed to influence the extent of the solubilization (38). The

The conclusion may be drawn from the aggregation equation

$$nMX \rightleftharpoons nM^+ + nX^- \rightleftharpoons (X_nM_m)^{-(n-m)} + (n-m)M^+$$

where MX is any 1-1 colloidal electrolyte, that additions of M^+ would tend to be unfavorable to aggregate formation, i.e., force the equilibrium to the left. If the extent of solubilization is dependent on the extent of the aggregation, electrolyte additions, according to the equation just presented, would tend to be unfavorable toward solubilization. The possibility of complex interactions makes prediction hazardous for any but dilute solutions, but the ionic strength concept might be useful in correlating the various data. Also, since the hydrophilic group of the solubilizing agent molecule must be highly hydrated, salt effects should be considered, with perhaps the lyotropic ranking of the various ions being a useful concept in treating the effect of electrolytes on the solubilization limit.

Nonelectrolytes added to the aqueous solution can likewise either increase or decrease the extent to which a given compound is solubilized. Ethanol (39), for example, decreases the ability of aqueous potassium oleate and potassium laurate solutions to solubilize the dyestuff Orange OT. Certain hydrocarbons, e.g., benzene and toluene, enhance the extent of the solubilization. The addition of straight chain alcohols (C_8-C_{12}) have been observed to increase substantially the extent to which n-heptane can be solubilized by aqueous 0.35M potassium myristate solutions (40-41). While the solubilization of mixtures of compounds is of practical importance, the status of the existing knowledge does not permit these effects to be simply explained, although certain investigations do indicate that the added materials alter the aggregation process (42).

Temperature effects have not been extensively studied. For the several solid dyestuffs (35, 43, 44), increased quantities were solubilized at elevated temperatures; these data were reported for two temperatures (30 and 60°C.). Hutchinson, et al., (45) studied the effect of temperature on the solubilization of n-hexyl and n-heptyl alcohols in aqueous sodium decyl sulfate solutions. Temperature and concentration effects were found to be interrelated and no detailed analysis was given, but, in general, higher temperatures favored increased solubilization for the polar compounds studied. For hydrocarbons, higher temperatures were unfavorable. In these experiments the temperature was varied over the 25-55°C. range.

A recent monograph by Hutchinson and M.E.L. McBain (23) reviews almost all of the published data concerned with the solubilization phenomenon. A more concise review was presented in 1950 by Klevens (46).

PRESENTATION OF PROBLEM

In the past, the solubilization phenomenon has been treated almost exclusively in an empirical manner. Because so little is known about the fundamental aspects of the process, no quantitative treatment has been possible. This situation has developed largely because of our incomplete understanding of the nature of aqueous solutions of association colloids.

According to the classical theory considered to apply to solutions of association colloids, a preferred size for the aggregate exists above a fixed critical concentration. Although solubilization data may frequently be interpreted qualitatively in terms of these concepts, the latter are not adequate bases for quantitatively describing the process. While the classical theory cannot be summarily rejected, caution should be exercised in basing interpretation on this concept entirely.

In order to describe the solubilization process more quantitatively, more information regarding the aggregation phenomenon must be obtained. The possibility exists that solubilization measurements themselves may give information regarding the nature of the aggregation existing in solution. By logically relating the association and the solubilization phenomena, a more exact description of both processes might be obtained.

In the present study, an attempt will be made to utilize solutilization data as a tool for studying the association phenomenon. Through an expansion of information regarding the association phenomenon a more quantitative description of the solubilization process should be possible. Two solubilizing agents, one ionic and one nonionic, will be investigated. Two variables

which should *a priori* be involved, the concentration of the solubilizing agent and the temperature, will be explored. The effect of temperature on the solubilization of even the relatively simple compounds commonly employed in studies of this type has been investigated in only a cursory manner. The effect of the concentration of the solubilizing agent solution has been restricted largely to solutions more than 0.1*M* in the solubilizing agent. In this work this concentration will be the upper limit.

Because the solubilization process conceivably could be important in the deresination of nonalkaline pulps, the experimental materials to be used in this study have been selected in such a manner that some indication of the role of solubilization in the deresination process might be obtained.

EXPERIMENTAL PROCEDURES

METHOD OF DETERMINING THE SOLUBILIZATION LIMIT

DEVELOPMENT OF METHOD

In considering methods of determining the phase relationships for systems in which solubilization occurs, it should be recalled that these systems are similar to those in which ordinary solution phenomena occur and that the same disciplines apply to both systems. Obviously, complete phase diagrams for the systems of interest can be prepared only if the phases in equilibrium are isolated and analyzed. If a particular phase boundary is to be located, i.e., the locus of saturated compositions, this usually can be accomplished by plotting, isothermally, the value of some property of the system as a function of the total composition of the system. For example, with the system lauric acid-potassium laurate-water (Figure 1), any properly selected property of this system should vary regularly with respect to the total composition of the system as long as the aqueous solution remains unsaturated with lauric acid (from C to P). A break in the plot may then be used to determine the composition of the saturated liquid, or in this case, the amount of lauric acid solubilized by a solution of potassium laurate of a fixed concentration.

The property selected in making this type of determination depends on the nature of the system being studied. With the usual liquid-liquid system, i.e., in ordinary solubility measurements, a turbidimetric method may be satisfactorily employed. When one liquid phase becomes saturated with

another, a visible turbidity develops because of the different optical properties of the two phases, assuming that the second or separating phase is mechanically dispersed in the system.

This technique has been adopted for making solubilization limit determinations (33). These determinations are made by adding different amounts of solubilizate to vessels containing fixed volumes of an aqueous solubilizing agent solution and subjecting the containers to vigorous agitation, isothermally, for extended periods of time. These systems may then be either visually or instrumentally observed to determine the amount of solubilizate required to saturate the aqueous solution. This is a satisfactory procedure but is time consuming.

Any of the more common means of preparing dispersions used by the colloid chemist might be applied with advantage to these systems. Because an ultrasonic generator (General Electric 8665966G3) was available, attempts were made to disperse the solubilizate with this apparatus, and dispersion proved to be rapid and efficient.

The success of this technique suggested a possible alternative means for making the solubilization limit determination. In considering this method, the phase diagram (Figure 1) should be examined. The conventional method involves the addition of pure lauric acid (A) to an aqueous laurate solution, of concentration C, for example. The final over-all composition of the system must lie along AC, point P being the composition desired. This same point on the boundary could also be determined by mixing a suspension of over-all composition X with C. Such a procedure would possibly

enable the determination to be made volumetrically, only a single weighing of the solubilizate being required in preparing the suspension X.

To determine if these measurements could be conducted in an approximately continuous manner, a photometer was constructed with which the turbidity of the system could be determined isothermally at the elevated temperatures to be employed (the photometer design will be discussed later). In the initial experiments, sodium tetradecyl sulfate was the solubilizing agent. Both oleic acid and dodecyl alcohol were used as solubilizates. Measurements were made at 50 and 70°C.

The limit determinations were made by successively adding aliquots of a suspension, prepared ultrasonically, to a given volume of the solubilizing agent solution (corresponding to X and C in Figure 1). The contents of the cell in which the determination was carried out were continuously stirred, and the turbidity of the system recorded as a function of time. At the temperatures of these experiments, the systems equilibrated rapidly, 10 minutes being the maximum time required after each addition of the suspension.

Attempts were also made to reverse this procedure, i.e., add the aqueous solubilizing agent solution to the suspension. This procedure was unsatisfactory because at high temperatures, particularly with the systems in which sodium tetradecyl sulfate was used as the solubilizing agent, the second phase tended to coagulate, even with stirring. This caused the turbidity of the suspension to decrease continuously on standing.

With the method evolved previously, this latter effect was not noted because the over-all system was always dilute with respect to the added

suspension. In fact, when the suspension was ultrasonically agitated before each addition, the transmission-concentration relationship in the two-phase region could be reproduced almost exactly.

TURBIDIMETER DESIGN

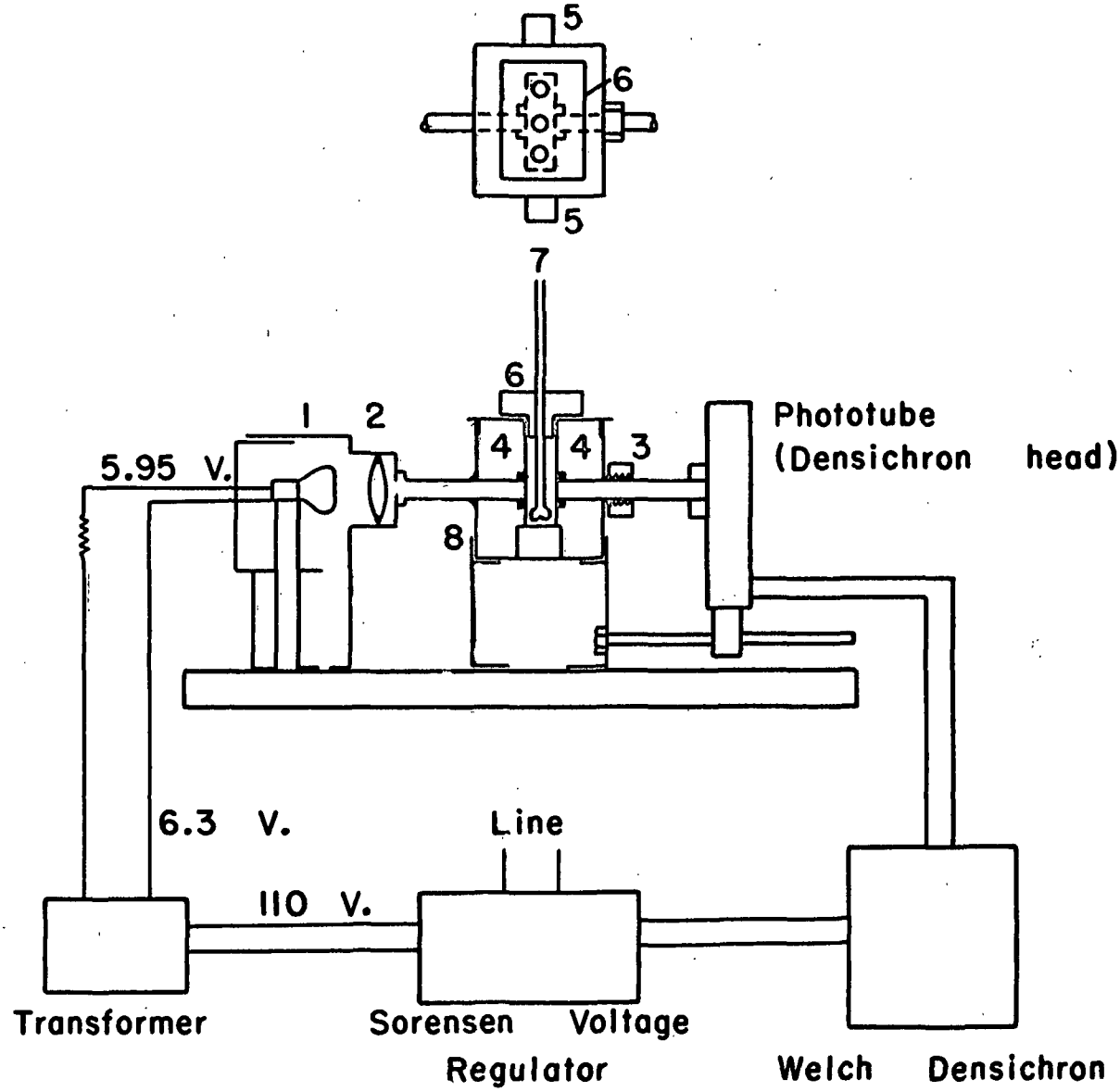
None of the common instruments for measuring the turbidity of liquids are equipped with the necessary accessories to permit measurements to be made isothermally at elevated temperatures. In order to make determinations under these conditions, the photometer shown in Figure 5 was constructed.

The only feature of this device which differed from the usual transmission-type turbidimeter was the jacketed-cell which contained the test liquid. This jacket was fabricated from copper sheet. The openings to either side of the pyrex cell were made of copper tubing. Rubber gaskets were used against the cell faces. A compression fitting was used on one side of the cell. A fitting of this type allowed the cell to be easily removed for cleaning and provided a good seal against the cell.

Either water or glycerol was pumped through the jacket from a reservoir maintained at the desired temperature with mercury regulators.

The light source was a 50 cp. 6-8 v. lamp operated from a regulated power supply at 5.95 v. A collimating lens and stop were affixed to the lamp housing. A Welch Densichron (phototube with S-4 response and linear meter) was used to determine the intensity of the transmitted beam.

Pyrex cells measuring 4 by 5 cm. with a 1.00-cm. optical path were used. The cell was covered with a tight fitting rectangular rubber lid fitted into



1 6-8 V. lamp
2 Collimating lens and stop
3 Compression fitting (Seal)
4 Seals at cell faces
5 Entrance and exit ports for heat transfer medium
6 Rubber cell cover containing openings for stirrer, thermometer, and access
7 Stirrer
8 Cell jacket

Figure 5. Schematic Diagram of Apparatus Used for Solubilization Limit Determinations

the cell opening in the metal cover of the jacket. Into the rubber cell lid, two holes were bored to permit a thermometer and the stirrer shaft to be inserted into the cell. A third opening was made to enable liquid additions to be made to the cell. When not in use, this latter opening was tightly stoppered.

SOLUBILIZATION LIMIT DETERMINATION--LIQUIDS

The suspension used in determining the solubilization limit for liquid solubilizates was prepared by adding a weighed amount of the solubilizate (weighed in a glass capillary) to 25.00 ml. of the aqueous solubilizing agent solution in a test tube. To eliminate possible oxidation of any component of the system during the ultrasonic agitation, the air in this test tube was replaced by nitrogen. The tube was then stoppered and suspended in the sound chamber of the ultrasonic generator.

The time required to completely disperse the solubilizate depended on the material being dispersed and on the power input. Since the adsorption of the sonic energy by the liquid caused the temperature of the suspension to increase, short interrupted periods of exposure were employed rather than extended exposures. This permitted the temperature to remain near the level at which the experiment was to be conducted. When the dispersing operation was completed, the suspension was placed in a water bath at the desired temperature.

In making the limit determination, 5 to 7 cc. of aqueous solubilizing agent solution were pipetted into the cell. The cell cover was put in place and the stirrer started. When temperature equilibrium was attained, additions

of the suspension were made through the opening in the cell cover by means of a 1-ml. graduated pipet with 0.01-ml. graduations.

In almost all instances, a rough orienting determination served to determine the approximate solubilization limit. On the basis of this determination, the subsequent measurement could be refined.

The actual meter reading was recorded as a function of the total system composition. The mass ratio of the solubilizate to the solubilizing agent was conveniently employed since all solutions and suspensions had been prepared gravimetrically. A typical curve is given in Figure 6. In all instances, the initial additions of the suspension were controlled so that one or more points in the homogeneous region of the phase diagram were obtained. The turbidities of the solubilized systems were not significantly different from those of the blank solubilizing agent solutions. The limit was determined by extrapolating the meter reading-concentration curve to the meter reading of the blank solubilizing agent solution as shown in Figure 6.

SOLUBILIZATION LIMIT DETERMINATION--SOLIDS

In determining the extent to which solids were solubilized, the procedure used for liquids was not directly applicable because of the time required for these systems to equilibrate.

Solids were weighed in a microbeaker and added to a known volume of the solubilizing agent solution. Ultrasonic radiation was used to prepare finely divided suspensions of the solid in the aqueous solution. In some cases, suspensions containing solid in excess of the solubilization limit

presented a smectic appearance. Excess solid in other instances appeared in the free state.

Varying amounts of the prepared suspension were added to test tubes containing fixed volumes of the solubilizing agent solution. These were tightly stoppered and placed in the constant temperature bath, the test tubes being periodically removed and subjected to ultrasonic agitation. Transmission measurements were made individually on the contents of each test tube at the temperature of the bath, equilibrium being established in 3-4 hours. Even though the turbidity of these systems was due in some cases to the finely divided solid present in excess of the quantity solubilized, the limit could be determined in the same manner as with the liquid solubilizates. Good stirring was required throughout the measurements to keep the solid in uniform suspension. This procedure could not be used unless the solid was finely divided. To minimize errors which theoretically could arise through adsorption of the solubilizing agent by the excess solid, the measurements were made very near the limit. This required the running of a preliminary experiment to gain an approximate value of the limit.

SYNTHESIS OF SODIUM TETRADECYL SULFATE

With only minor variations, the method used for preparing the sodium tetradecyl sulfate was that recommended by Dreger and co-workers (47). Chlorosulfonic acid is used in this procedure as the sulfating agent. The reaction takes place according to the equation:

$$ROH + ClSO_3H \longrightarrow ROSO_3H + HCl.$$

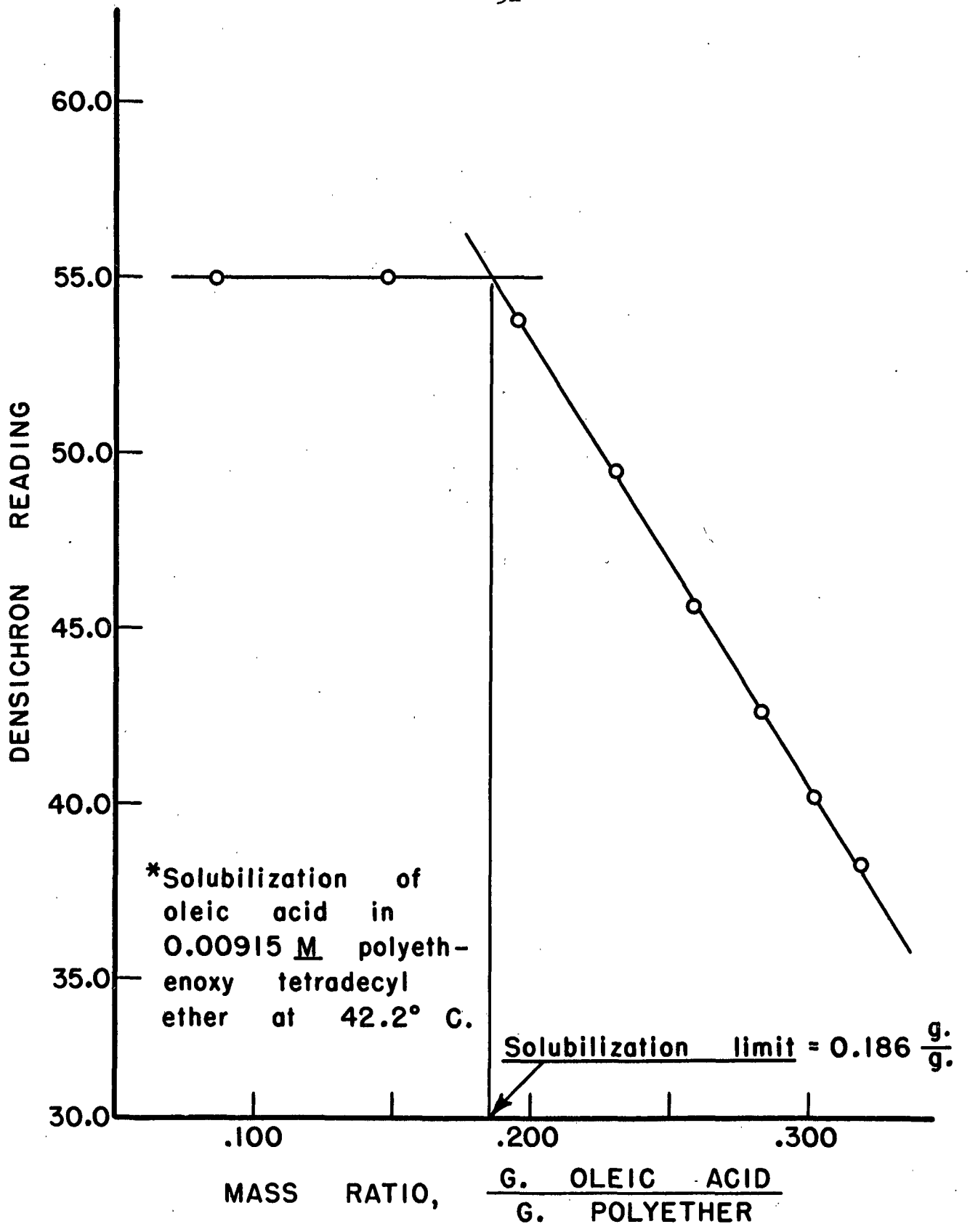


Figure 6. Typical Plot* for Determining the Solubilization Limit

The HCl escapes as a gas. The sulfuric ester formed is neutralized to give a product containing very little inorganic salt.

To a sulfating mixture composed of 200 g. of glacial acetic acid and 120 g. chlorosulfonic acid at 5°C., 200 g. of n-tetradecyl alcohol were added. The alcohol was added in the molten state, the mixture being vigorously agitated. The rate of addition of the alcohol was such as to maintain the temperature at or near 5°C. (about twenty minutes were required to add all the alcohol). Thereupon, the reaction mixture was stirred for thirty minutes in a cracked ice bath.

At the end of the reaction period, the reaction mixture was poured into 600 cc. of n-butanol containing 600 g. of cracked ice. This mixture was then neutralized with 2N sodium carbonate keeping the mixture saturated with sodium bicarbonate. On standing, two phases are formed. The sodium tetradecyl sulfate was retained largely in the butanol-rich layer of the system (the lighter phase). This layer was removed by decantation and concentrated. Any inorganic salts present precipitate during this concentration process and were removed by filtration.

When the concentrated butanol solution was cooled to room temperature, the sodium tetradecyl sulfate readily crystallized from the solution and was collected by filtration. The crystalline material was again taken up in hot butanol and reconcentrated to assure removal of any inorganic salts. After recrystallization, the sulfate was taken up in water and the aqueous solution concentrated under vacuum to remove any butanol present. The sulfate crystallized from the aqueous solution at room temperature (25°C.).

The crystalline material, removed by filtration, was washed with absolute ethanol and dried under vacuum at 50°C.

To remove any unreacted alcohol, the dried crystalline material was extracted with low boiling petroleum ether (b.p. 30-60°C.) in a Soxhlet extractor for 4 hours. The extracted material was subsequently recrystallized three times from a hot ethanol-methyl ethyl ketone mixture and finally dried at 50°C. under vacuum for 24 hours. The final product was a white crystalline solid which decomposed when heated above 150°C. Dilute aqueous solutions of this compound were neutral.

SYNTHESIS OF POLYETHENOXY TETRADECYL ETHER

The nonionic solubilizing agent used in this study was prepared by causing ethylene oxide to react with n-tetradecanol. Ethylene oxide adds to hydroxyl groups under relatively moderate conditions according to the equations:

$$ROH + CH_2\text{-}CH_2 \longrightarrow ROC_2H_4OH \text{ (First mole of ethylene oxide)}$$

$$ROC_2H_4OH + CH_2\text{-}CH_2 \longrightarrow ROC_2H_4OC_2H_4OH \text{ (Second mole)}$$

$$ROC_2H_4OH + n\ CH_2\text{-}CH_2 \longrightarrow ROC_2H_4(-OC_2H_4-)_nOH \text{ (n+1 moles)}$$

Many of the more common nonionic detergents are prepared by this reaction, usually from fatty alcohols or alkylaryl phenols.

In the laboratory, the reaction was conveniently conducted using 100 g. of n-tetradecanol (Matheson, Coleman and Bell, m.p. 36-38°C.) to which 0.1 g. potassium hydroxide was added as a catalyst. The reactor consisted of a tared 500-ml. three-necked flask equipped with gas inlet and outlet ports, a

motor-driven stirrer, and thermometer. The reactor was heated by a rheostat-controlled mantle. The alcohol was heated to 170°C. and gaseous ethylene oxide (Matheson Company, 99% pure) was admitted through a gas disperser beneath the surface of the molten alcohol. The reaction mixture was vigorously stirred throughout the entire reaction period. The temperature was maintained at 170 ± 5°C. The extent of the reaction was determined periodically by weighing the reactor and its contents. Care was exercised on these occasions to flush the system with nitrogen and to maintain this environment during the weighing operation because exposure to air at these temperatures caused marked changes in color of the reaction mixture. When the system was protected, the final product was essentially colorless in the molten state.

The particular product prepared for the work to be described contained 3.13 parts (by weight) of ethylene oxide per part of n-tetradecanol. An average molecular weight of 884 (based on the weight of ethylene oxide gained) was calculated for this material. The time required to prepare this product (excluding the down time for weighing) was approximately 8 hours. The final product was a white waxlike solid at room temperature. Dilute aqueous solutions were slightly acid (pH of 6.90-6.95).

During the initial phases of this study, the discovery was made that even dilute solutions of nonionics of the types to be used were unstable at elevated temperatures. The nature of this instability and the subsequent stabilization of these solutions is discussed in APPENDIX I. Data establishing the reproducibility of the reaction conditions are also presented in APPENDIX I.

The laboratory procedure used for preparing the nonionic solubilizing agents was obtained, through private communications, from Dr. J. V. Karabinos of the Blockson Chemical Company, Joliet, Illinois, and from Dr. J. E. Ward of the Nopco Chemical Company, Harrison, New Jersey.

SOURCES AND PURITIES OF EXPERIMENTAL MATERIALS

Abietic Acid. Hercules Powder Company, Wilmington, Del. (Dr. G. C. Harris). m.p. 171-3°C.

n-Octadecanol. Matheson Company, Inc., Norwood, Ohio. m.p. 56-8°C.

Oleic Acid. Mann Research Laboratory, New York 6, N. Y. 99% purity.

β-Sitosterol. Isolated by repeated recrystallizations (methanol) from "Tall Oil Sterols" supplied by the Industrial Chemical Sales Division, West Virginia Pulp and Paper Company, 230 Park Ave., N. Y. 17, N. Y.

This material was supplied with the following analysis:

85% β-sitosterol
10% sitostanol
5% water
Traces lignoceryl alcohol.

After four recrystallizations, a material melting at 135-6°C. was obtained. The melting point was not altered by further recrystallizations from methanol.

Stearic Acid. Matheson Company, Inc., Norwood, Ohio. m.p. 69-70°C.

n-Tetradecanol. Matheson Company, Inc. m.p. 36-8°C.

Trimyristin. Matheson Company, Inc. m.p. 55.5-6.0°C.

PRESENTATION AND INTERPRETATION OF EXPERIMENTAL RESULTS

THE SOLUBILIZATION OF OLEIC ACID AND n-OCTADECANOL BY AQUEOUS SOLUTIONS OF POLYETHENOXY TETRADECYL ETHER

The extents to which oleic acid and n-octadecanol could be solubilized by aqueous solutions of polyethenoxy tetradecyl ether (mol. wt. 884) were determined over a concentration range of the solubilizing agent extending from 0.00152M to 0.0215M (i.e., from about 0.14 to 1.9%, by weight). The influence of temperature on the solubilization of these compounds was studied over this composition range at temperatures ranging from 43 to 73°C. for oleic acid and from 57 to 73°C. for n-octadecanol. Under the conditions of these experiments, both compounds were solubilized from the liquid state. The data are presented in Table I.

Over the concentration and temperature ranges investigated, the solubilization limits for both oleic acid and n-octadecanol were independent of temperature. The solubilization limits for these compounds were observed to increase almost linearly with the concentration of the solubilizing agent solution as shown in Figure 7. Over the range studied, oleic acid was solubilized in slightly larger amounts than n-octadecanol.

The relationship between the amount of material solubilized and the concentration of the solubilizing agent solution (Figure 7) obtained from these experiments appeared in the expected form. Classically, this relationship is explained by assuming that all of the solubilizing agent added in excess of the critical concentration is in the aggregated state. Assuming that each aggregate has the same capacity for "binding" the solubilizate, the

TABLE I

SOLUBILIZATION LIMITS OF OLEIC ACID AND n-OCTADECANOL IN AQUEOUS SOLUTIONS OF POLYETHENOXY TETRADECYL ETHER

Molarity of Solubilizing Agent	Solubilizate	Temp., °C.	Solubilization Limit	
			g. Solubilizate / g. Solubilizing Agent	Moles[a] / Liter
0.00152M	oleic acid	56.9	0.175	
		65.9	0.175	0.000835
		73.2	0.175	
0.00498M	oleic acid	42.3	0.182	
		56.9	0.183	0.00284
		65.2	0.183	
		73.6	0.181	
0.00916M	oleic acid	42.2	0.186	
		56.9	0.186	0.00532
		65.4	0.186	
		73.3	0.186	
0.0208M	oleic acid	45.3	0.194	
		57.0	0.193	0.0126
		65.1	0.192	
		73.2	0.192	
0.00152M	n-octadecanol	57.0	0.153	
		73.2	0.153	0.000764
0.00494M	n-octadecanol	57.0	0.165	
		65.5	0.161	0.00263
		73.2	0.162	
0.00916M	n-octadecanol	56.9	0.172	
		65.5	0.174	0.00520
		73.2	0.172	
0.0215M	n-octadecanol	56.9	0.185	
		65.7	0.186	0.0131
		73.2	0.187	

[a] $\frac{\text{g.}}{\text{g.}}$ values averaged in calculating moles/liter values.

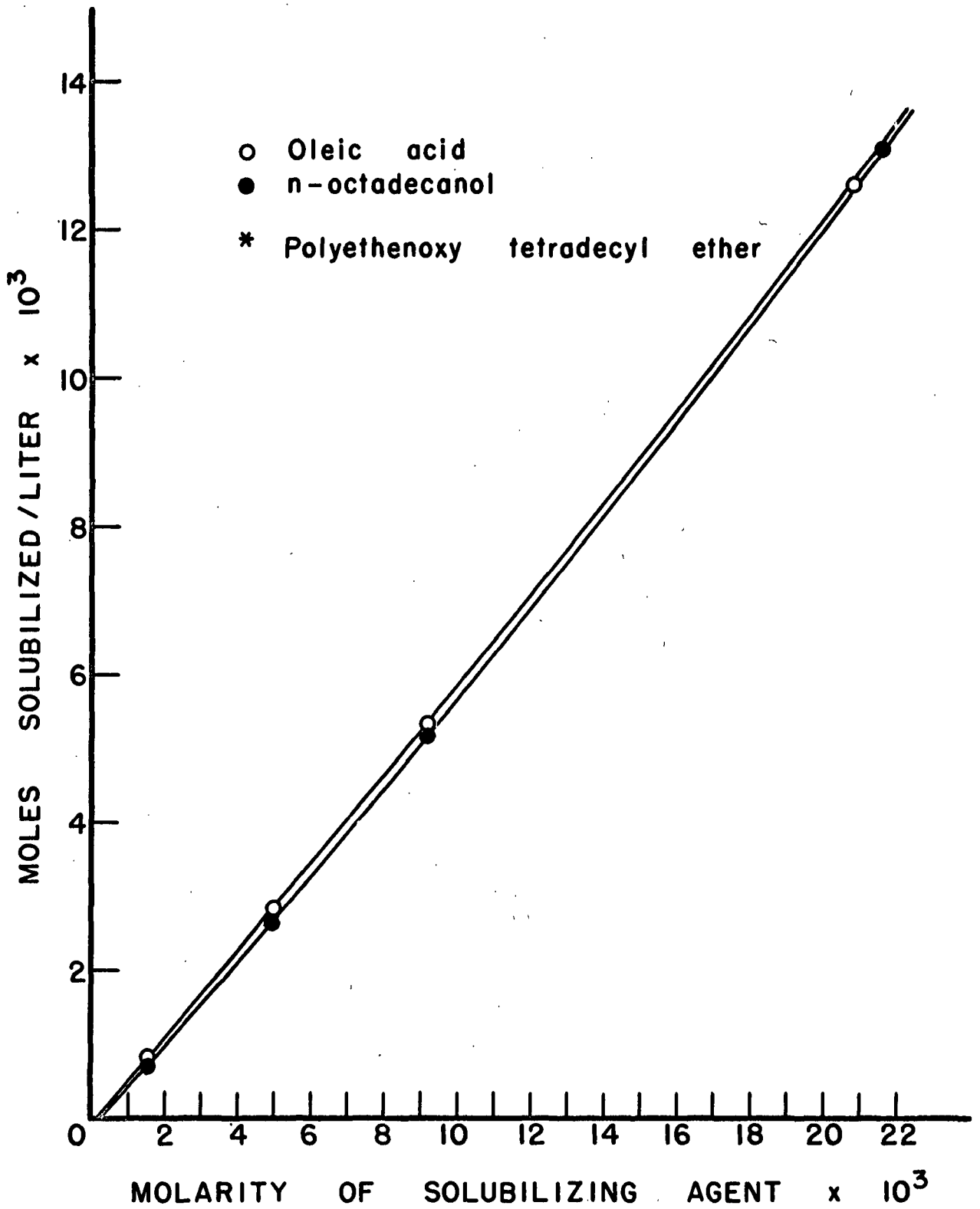


Figure 7. Relationship Between the Amount of Material Solubilized and the Concentration of the Solubilizing Agent* Solution

conclusion is drawn that above the critical concentration the solubilization limit for a given compound varies directly as the concentration of the solubilizing agent solution. Although this explanation enables the experimental data to be partially interpreted, the assumptions made lack verification. Actually, the relationships shown in Figure 7 are not linear, being in this case slightly convex toward the abscissa. In a later section this relationship will be discussed in detail.

The absence of any temperature influence on the solubilization limit over the investigated range was unexpected. The meager information regarding the effect of temperature on the solubilization limit of liquid which has been reported pertains only to ionic solubilizing agents. [When polar compounds were solubilized by ionic agents, both positive and negative temperature effects were observed, depending on the concentration of the solubilizing agent (44, 45).]

Accepting the theory that the solubilized compound is in some way associated with the aggregated fraction of the solubilizing agent, knowledge of temperature effects on the aggregation process should be useful in explaining such effects (or their absence) observed in the solubilization process. In the absence of specific information, attention must be directed to the energetics of aggregate formation.

With ionic association colloids, the principal forces active in "binding" the aggregate together must arise from the van der Waals attractive forces between the hydrocarbon chains of the aggregate. At elevated temperatures, thermal effects would tend to destroy these low energy bonds. The destruction

of a portion of these bonds, coupled with the repulsive forces existing between the charged ionic heads of these molecules, would seemingly tend to decrease the extent of the aggregation. If this were the only change induced by increasing the temperature, the solubilization capacity of a solution of fixed concentration would be less at elevated temperatures, i.e., a negative temperature coefficient for solubilization should be observed. Other effects might also arise to offset the decreased extent of aggregation. The possibility exists that the polar ionic groupings of the solubilizate molecules would be more highly hydrated in a loose aggregate structure at higher temperatures (based on spatial considerations). An aggregate of this type would possibly be more efficient as far as solubilization is concerned.

With the nonionics of the ethylene oxide type, the hydrophilic portion of the solubilizing agent molecule is the polyethylene oxide chain. In aqueous solution this chain is highly hydrated. Kushner and Hubbard (48) have shown that each ether oxygen in the polyethylene oxide chain can bind a maximum of four water molecules. This situation is strikingly different from that encountered with ionic materials in that the terminal polar groups are not charged and hence no electrical repulsive forces exist between the terminal groups when aggregates are formed.

In considering the effect of temperature on aggregates formed from the nonionic compounds, attention must be given to the effect of temperature on the hydrophilic portion of these compounds. Karabinos (49) has shown that the extent of the hydration of this chain increases with increasing temperature, up to a certain temperature. Raphael (50) has deduced, from viscometric

studies, that interlocking of the highly hydrated chains occurs when the polyethylene oxide chain is long. On the basis of those observations, a rather simple theory regarding the influence of temperature on the aggregation of these materials can be presented.

If the interlocking between the long hydrophilic chains is considered, these interactions would augment the attractive forces existing between the hydrocarbon portions of the aggregated molecules, tending to stabilize the aggregate toward thermal disrupting influences. At temperatures below that necessary to break the bonds between the water molecules and the ether oxygen atoms of the polyether chain, the aggregate should be relatively stable to moderate temperature changes if the molecules comprising the aggregate possess long polyethylene oxide chains. This would be the case if it is assumed that a fixed number of bonds between chains can effect stability. Thermal agitation would cause the scission of an increasing number of these bonds as the temperature is increased, but would only be detected when the existing number of bonds were reduced below some minimum value.

If the aggregate size remained essentially constant over a given temperature range, the solubilization capacity of a solution of fixed concentration might also be expected to be unaltered by temperature variations over the same range. The experimental results are in accord with this theory.

In making the experimental determinations, suspensions containing 2 to 2 1/2 times the limit value were prepared. These suspensions, after ultra-

sonic agitation, exhibited an opalescent appearance typical of very finely divided suspensions. On standing, the dispersed phase tended to coagulate and settle out of the aqueous phase. This separated phase appeared homogeneous under white light and isotropic under polarized light. Since this material settled from the aqueous phase present, the conclusion may be drawn that this separating phase is not pure solubilizate, since both solubilizates were less dense than the aqueous phase in the pure state. This situation appears similar to that exhibited by the three-component system in Figure 1. The solubilized phase exists in equilibrium with an isotropic phase rich in the compound being solubilized and the solubilizing agent. This occurs at low concentrations of the solubilizing agent.

THE EFFECT OF ADDED ELECTROLYTES ON SOLUBILIZATION

Kushner and Hubbard (48) and Karabinos (49) have shown that the polyethylene oxide chain of nonionics of the types of interest in this work are highly hydrated in aqueous solutions. Thus, aggregates of these materials may be pictured as possessing a shell of bound water around their outer surfaces. The solubility of the aggregate is undoubtedly due largely to the over-all interaction between the polyethylene oxide chain and the water, and, in the first approximation, factors which alter the extent of the chain hydration might be expected to alter the solubility of the aggregate. By purely qualitative reasoning, factors which would alter the solubility of the aggregate would be expected to influence the extent to which a given material could be solubilized by the aggregate.

Aggregates of these compounds in solution might be expected to behave

similarly to neutral hydrophilic sols. Hydrophilic sols are considered to possess a relatively thick shell, a lyosphere of loosely bound water. The extent of hydration, i.e., the thickness of this shell can be altered in a number of ways. Electrolytes, certain polar nonelectrolytes, and elevated temperatures all tend to diminish the extent of the hydration of a number of hydrophilic sols. If the extent of the hydration falls below a certain point, the dispersed phase is actually thrown out of suspension, i.e., salted-out. Combinations of heat and an electrolyte are commonly required for salting-out stable hydrophilic sols.

If the analogy presented is valid, the addition of strong electrolytes to the aqueous nonionic solubilizing agent might be expected to decrease the extent of the hydration of the aggregates, i.e., diminish the over-all hydrophilic properties. A diminution of the hydrophilic properties of the aggregate should be reflected in the ability of the aggregate to solubilize a given compound.

The effectiveness of ions in the dehydration of hydrophilic sols has been systematically studied and the various ions ranked according to the dehydrating properties exhibited, this tabulation being the familiar Hofmeister of lyotropic series. Each ion listed in the series is assigned a numerical value (59), the lyotropic number, which varies directly with the relative dehydrating ability of the ion. For the monovalent alkaline series, these numbers are: Li^+, 115; Na^+, 100; K^+, 75; and Cs^+, 60.

At a fixed ionic strength of the added electrolyte, those cations with the larger lyotropic numbers would be expected to be more effective in

dehydrating the polyethylene oxide chain than those cations at the bottom of the series. If the degree of hydration of the aggregate is an important factor influencing the extent of the solubilization of a given compound, the observed solubilization limits for a given compound would be expected to vary in a logical manner, i.e., inversely with the lyotropic number, when the different cations were present. A simple experiment was designed to test this reasoning.

Solutions, all 0.00498M in polyethenoxy tetradecyl ether, were prepared which were 0.100N in NaCl, LiCl, KCl, and CsCl. The extent to which oleic acid was solubilized by each of these solutions was determined at 63.0°C. The data obtained are presented in Figure 8, the solubilization limits being plotted as a function of the lyotropic number of the added cation. Although the data obtained from this abbreviated experiment do not prove the hypothesis presented, tentative support is given the contention that the extent of the hydration of the hydrophilic group of this nonionic solubilizing agent is a factor contributing to the solubilizing ability of this compound.

The possibility exists that temperature effects might become important in systems (of nonionics) containing electrolytes. The solubilization limits for oleic acid and stearyl alcohol were found to be independent of temperature over the range explored. This result was attributed to interactions between the highly hydrated polyether chains of the aggregate. If electrolytes diminish the extent of the chain hydration, below a certain degree of hydration these interactions would not be expected. Temperature effects might then be observed.

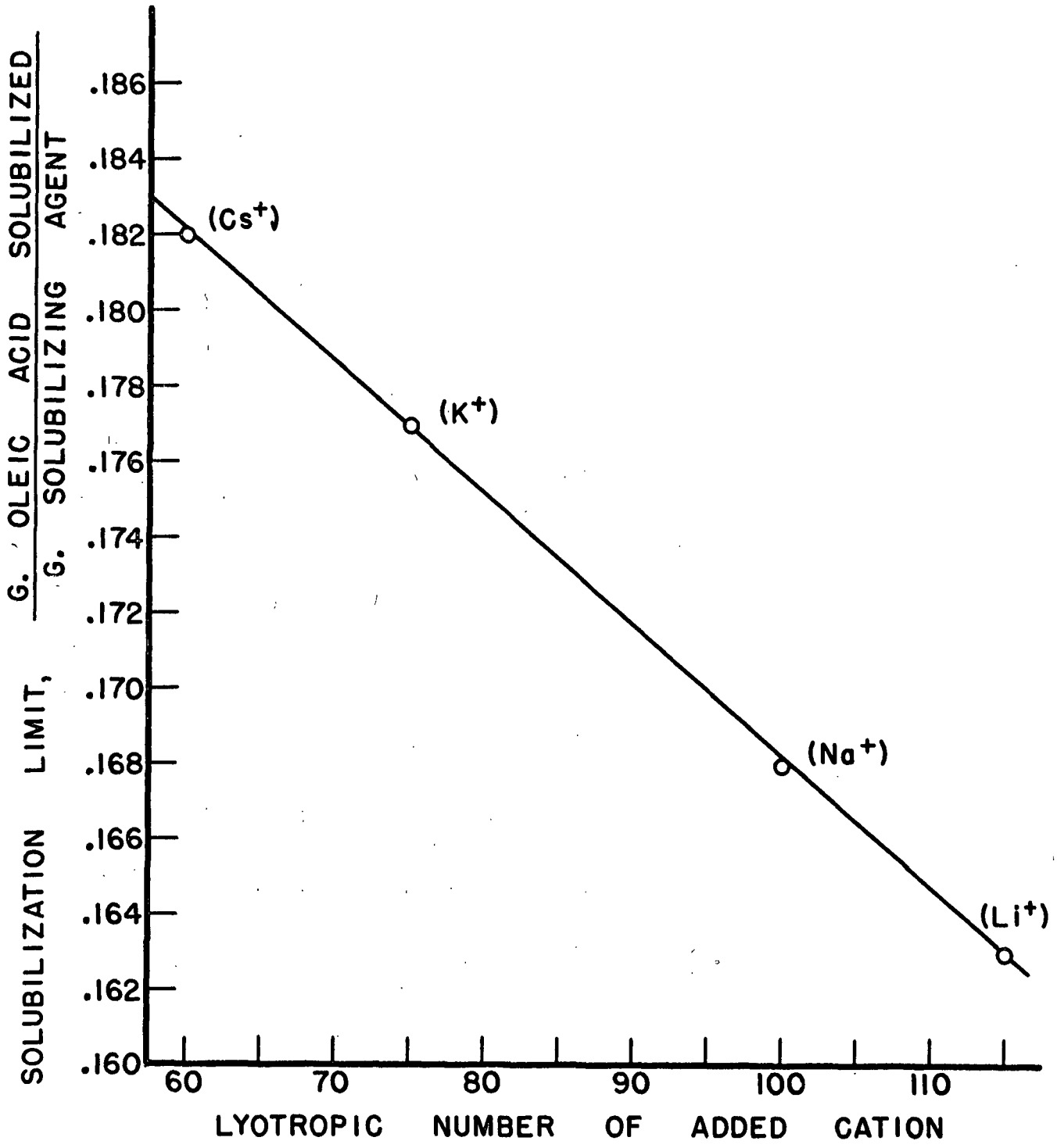


Figure 8. Relationship Between the Lyotropic Number of the Added Cation and the Solubilization Limit

No attempt was made to study this possibility in detail with the particular agent used in this work because of the length of the polyether chain. Three experiments were conducted, however, in which the solubilization limit of n-octadecanol was determined in solutions 0.00935M in the nonionic and 0.200N in NaOH at 56.7, 65.0, and 73.0°C. Under these conditions, the solubilization limit was still independent of temperature, being 0.0050 moles solubilized per liter of solution, as compared with a limit of 0.0052 moles per liter with no electrolyte at the same concentration of solubilizing agent. Here the solubilization limit was depressed 4% by the presence of the added caustic.

These experiments indicate that added electrolytes tend to unfavorably influence the effectiveness of the nonionic solubilizing agent, at least toward oleic acid and n-octadecanol.

THE SOLUBILIZATION OF n-OCTADECANOL AND OLEIC ACID BY AQUEOUS SOLUTIONS OF SODIUM TETRADECYL SULFATE

The solubilizing agent used in this series of experiments, sodium tetradecyl sulfate, resembled the nonionic previously employed in that the hydrophobic portions of both molecules were identical. The hydrophilic groups of the two compounds are, however, very different, the neutral polyethylene oxide chain of the nonionic being replaced by the sulfate group.

The extent to which n-octadecanol could be solubilized by aqueous tetradecyl sulfate solutions was determined over a concentration range extending from 0.00362M to 0.121M and over a temperature range extending from about 55 to 75°C. The solubilization limits are given in Table II. In Figures 9 and 10, solubilization isotherms are presented for the system. Both methods of plotting the solubilization isotherms are given because no definite convention has been established for presenting the results from solubilization experiments.

Referring to either Figure 9 or 10, the solubilization limits for this system are observed to be dependent on both temperature and concentration.. Beyond a concentration of about 0.013M, the solubilization limit increased when the temperature was increased. Below this concentration, solubilization was adversely influenced by temperature increases. At 55°C., the quantity of material solubilized was observed to vary almost linearly with the concentration of the solubilizing agent solution. At 65.0 and 75.0°C., the solubilizing agent apparently becomes less efficient when 0.008-0.010 moles of octadecanol/liter are solubilized (indicated by the attainment of

TABLE II

SOLUBILIZATION LIMITS

OLEIC ACID IN AQUEOUS SOLUTIONS OF SODIUM TETRADECYL SULFATE

Molarity of Solubilizing Agent	Solubilizate	Temp., °C.	Solubilization Limit, g. solubilizate / g. solubilizing agent
0.00362	oleic acid	45.3	0.160
		55.3	0.143
		66.7	0.122
		78.8	0.091
0.00605	oleic acid	45.3	0.193
		53.5	0.203
		65.0	0.233
		78.8	0.240
0.00665	oleic acid	55.5	0.210
		66.7	0.227
		78.8	0.246
0.00750	oleic acid	55.5	0.217
		65.0	0.254
		78.8	0.262
0.0121	oleic acid	45.3	0.222
		55.0	0.250
		65.0	0.272
		78.8	0.271
0.0241	oleic acid	44.5	0.205
		55.2	0.245
		64.4	0.267
		78.8	0.270
0.0420	oleic acid	44.5	0.158
		53.8	0.187
		65.1	0.215
		78.8	0.262
0.0825	oleic acid	46.0	0.154
		57.1	0.176
		65.0	0.198
		77.5	0.240

TABLE II (Continued)

SOLUBILIZATION LIMITS

OLEIC ACID AND n-OCTADECANOL IN AQUEOUS SOLUTIONS OF SODIUM TETRADECYL SULFATE

Molarity of Solubilizing Agent	Solubilizate	Temp., °C.	Solubilization Limit, g. solubilizate / g. solubilizing agent
0.121	oleic acid	45.6	0.173
		56.0	0.190
		67.2	0.212
		77.7	0.228
0.00362	n-octadecanol	54.0	0.052
		63.8	0.018
		78.8	0.000
0.00750	n-octadecanol	55.0	0.0969
		67.7	0.0801
		77.8	0.0600
0.0186	n-octadecanol	55.0	0.152
		67.8	0.162
		78.6	0.169
0.0425	n-octadecanol	55.0	0.168
		69.0	0.208
		77.8	0.219
0.0666	n-octadecanol	56.0	0.174
		65.0	0.201
		76.2	0.221
0.121	n-octadecanol	56.0	0.179
		66.0	0.191
		69.0	0.195
		78.0	0.204

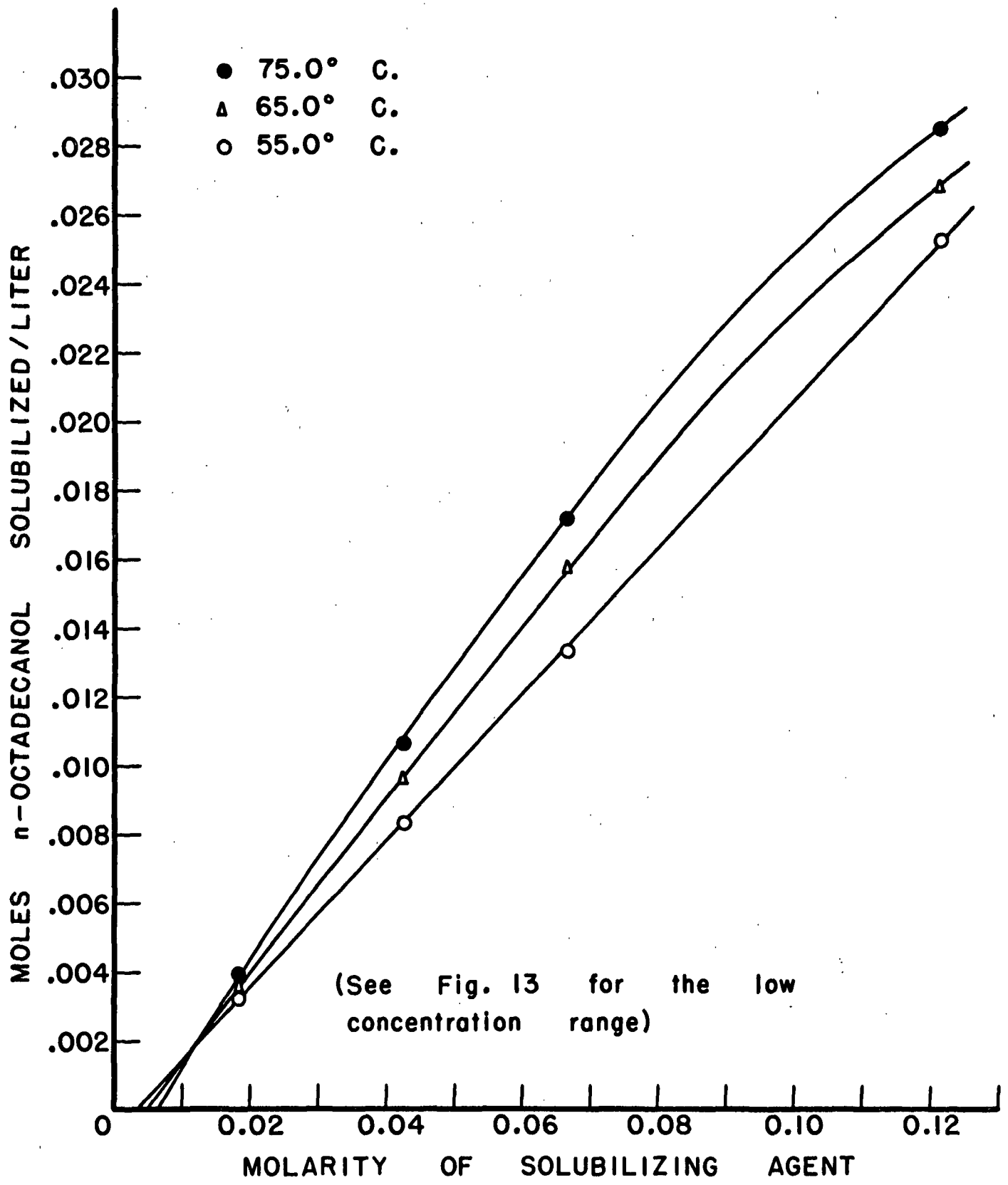


Figure 9. Effects of Temperature and Concentration of the Solubilizing Agent on the Solubilization of n-Octadecanol by Sodium Tetradecyl Sulfate Solutions

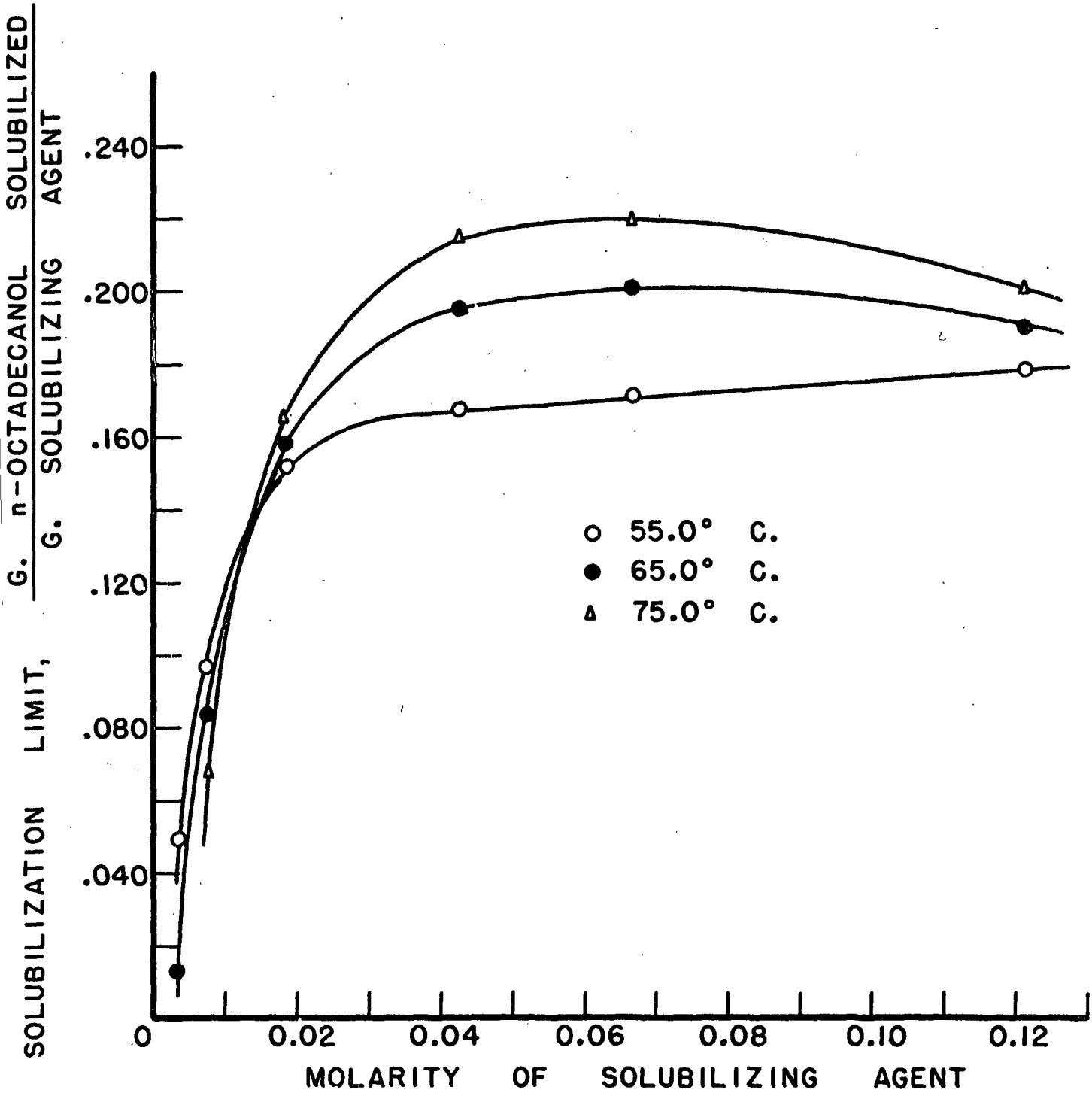


Figure 10. Effect of Temperature and Concentration on the Solubilization of n-Octadecanol by Sodium Tetradecyl Sulfate Solutions

the maximums at these temperatures in Figure 10 and by the fall-off to the right of the isotherms in Figure 9).

The solubilization limits for oleic acid were determined over the same concentration range, but over a broader temperature range (45-75°C.). Isotherms for this system are given in Figures 11 and 12 (data--Table II). In Figure 11, the solubilization limits have not been plotted at low concentrations of the solubilizing agent to avoid confusion in this region of the plot. The same type of temperature dependence is exhibited in this system as with that in which n-octadecanol was used as the solubilizate. The inversion point was observed at about 0.005M in the present system, whereas this occurred at 0.013M in the system in which oleic acid was used. The solubilizing agent appeared to become less efficient when 0.006 - 0.008 moles of oleic acid were solubilized, this range being slightly lower than that at which the same effect was observed when n-octadecanol was employed as the solubilizate. Under comparable conditions of concentration and temperature, sodium tetradecyl sulfate solutions were observed to be more effective in solubilizing oleic acid than n-octadecanol.

The temperature effects observed in both of these systems can be explained qualitatively by assuming that temperature brings about two changes in the aggregation process. Elevated temperatures would be expected to decrease the extent of the aggregation of the solubilizing agent. This would tend, particularly at low concentration, to decrease the effectiveness of the solubilizing agent solution. Elevated temperatures would also tend to "loosen" the structure of the existing aggregates thereby enabling the

hydrophilic end groups to become more highly hydrated. This would tend to increase the over-all hydrophilic properties of the aggregate, a factor which should enhance the solubilizing ability of the aggregate. Beyond a certain extent of aggregation this latter effect may be the more important. Above a given concentration, increased temperature should increase the solubilization limit. This matter will be reconsidered in a more quantitative manner in the next section of this thesis.

The reason why the solubilizing agent becomes less effective when a certain quantity of material is solubilized, isothermally, seems to be explainable in terms of the over-all aggregation process. In aqueous solution, the process of dissolution and aggregation may be represented by the equilibrium:

$$nMX \rightleftharpoons nM^{+} + nX^{-} \rightleftharpoons (X_nM_m)^{-(n-m)} + (n-m)M^{+}.$$

In this equation, MX can be any 1-1 colloidal electrolyte, e.g., sodium tetradecyl sulfate. In dilute solutions, the aggregates formed are assumed to consist largely of the negative charged anions. The polar hydrophilic groups are assumed to be highly hydrated. In addition to the bound water, the aggregate is closely associated with some number, m, of the related gegenions. The gegenions associated with the aggregate would be expected to control the extent of the hydration of the aggregate. In the first approximation, the ratio n/m would be expected to remain nearly constant. If this ratio remains fixed, the extent of the hydration of the aggregate may be assumed constant. If the hydrophilic character of the aggregate remained essentially constant, the solubilization limit, in the simplest case, would be expected to be an almost linear function of the solubilizing agent concentration.

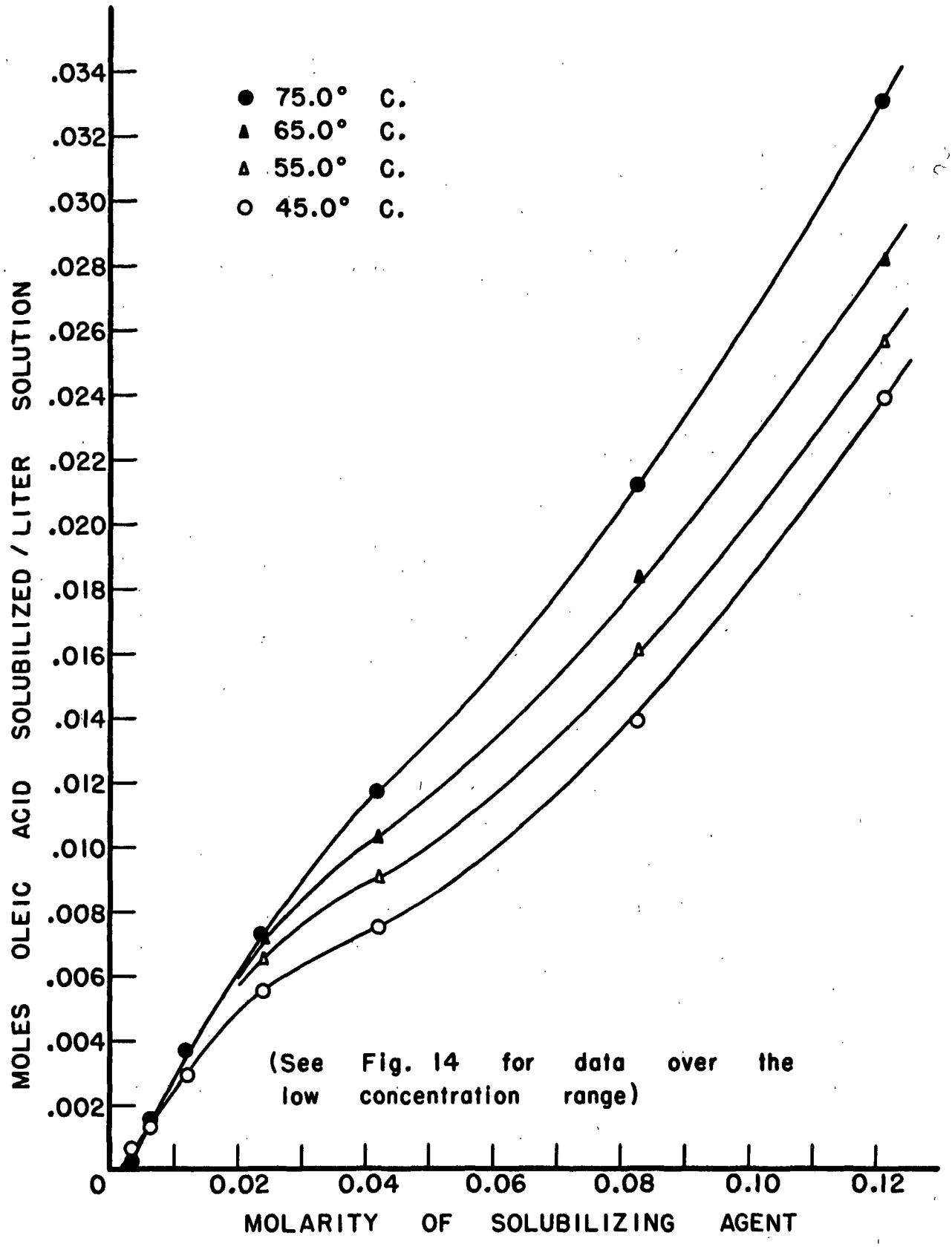


Figure 11. Effect of Temperature and Concentration on the Solubilization of Oleic Acid by Sodium Tetradecyl Sulfate Solutions

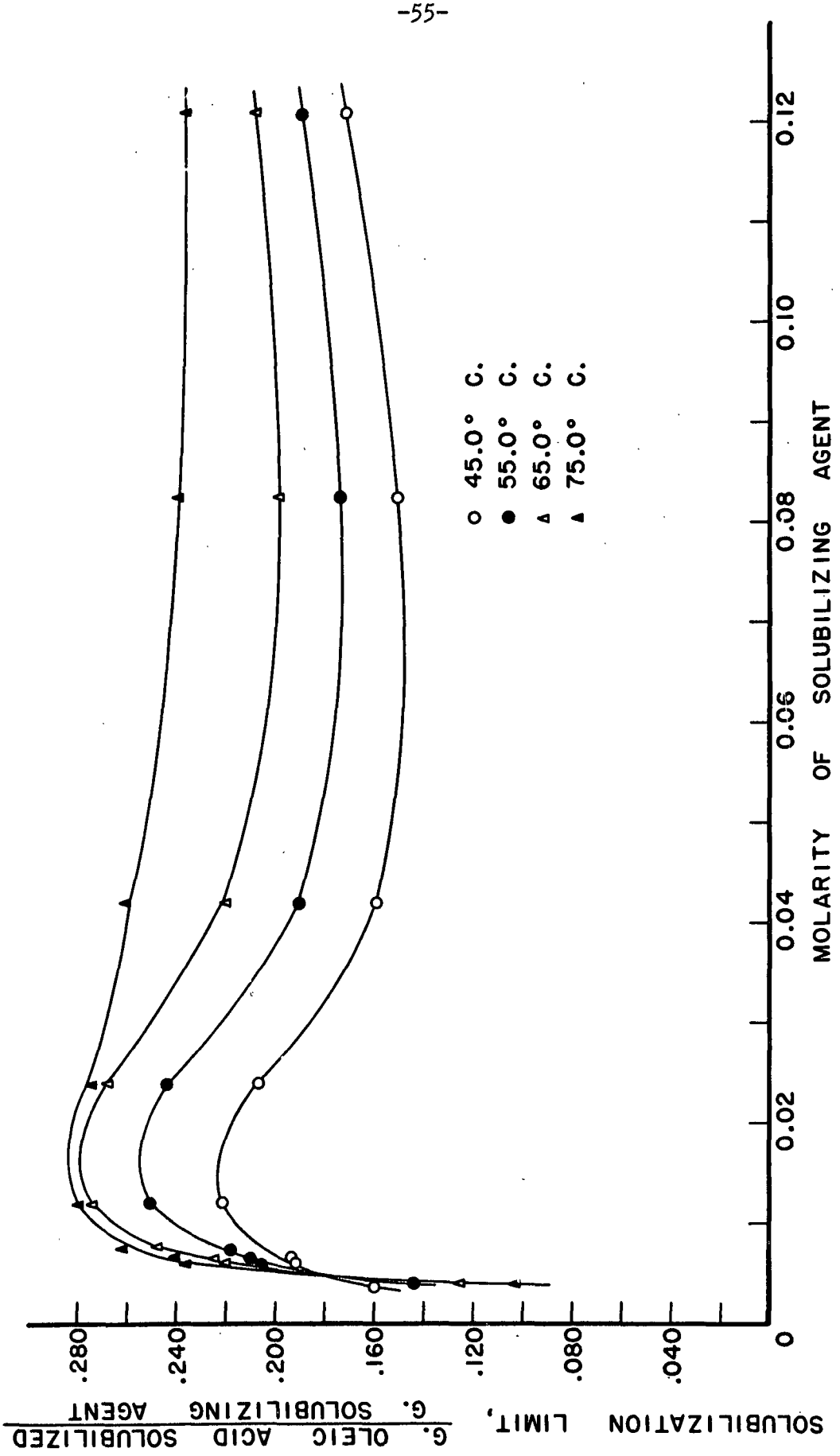


Figure 12. Effect of Temperature and Concentration on the Solubilization of Oleic Acid by Sodium Tetradecyl Sulfate Solutions

When solubilizate molecules enter the aggregate, the possibility exists that the number of gegenions associated with the aggregate may possibly be altered. The introduction of a polar group into the aggregate surface, which would occur in the solubilization of oleic acid, would yield new adsorption sites for the free cations in solution. The adsorption of additional gegenions by the aggregate would be expected to reduce the extent of the hydration of the aggregates in solution, causing an apparent reduction in the solubilizing ability of the aggregate. The polar character of the solubilizate should be a principal factor determining the extent of the additional adsorption of gegenions. Temperature would influence the extent of adsorption.

The aggregate size could also be a factor since, presumably, the force field causing the adsorption would be more uniform in the vicinity of a large aggregate. With large aggregates, the extent of the dehydration affected by the gegenions might then be more complete. In small aggregates containing only a few molecules of solubilizate, the adsorption and subsequent dehydration might be of secondary importance.

The actual experimental measurements were conducted as described in the EXPERIMENTAL PROCEDURES section. Suspensions containing solubilizate in excess of the limit appeared less stable than those prepared using the nonionic solubilizing agent. A gel-like phase settled from these suspensions quite rapidly, particularly at the higher temperatures. The separated phase was shown to be isotropic for both solubilizates. A smectic condition could be effected with the n-octadecanol suspensions. This was done by allowing a suspension prepared at a temperature above the melting point of n-octadecanol

to cool at temperatures well below the melting temperature. A more detailed study of the equilibrium diagram for this system would be required to determine whether or not a liquid crystalline phase actually exists in this system at low temperatures.

A POSTULATED MECHANISM

The experimental results which have just been presented have been treated in the manner typical of almost all reported solubilization studies. The experimental data have been graphed and analyzed in a purely qualitative manner. Quantitative analyses have not been given because no logical basis has been established for a more complete description of the solubilization phenomenon. No mechanism which can be seriously entertained has been presented regarding the manner in which a compound becomes solubilized.

In attempting to lend a more fundamental interpretation to the data obtained in this study, a physical picture or model has been conceived for describing the process by which solubilization is effected. Utilizing this model, a quantitative definition can be given to the system parameters. This treatment will be presented in the following text and the data previously discussed will be re-examined in the light of this presentation.

QUALITATIVE CONSIDERATIONS

Solubilization, in this discussion, will be considered as an interfacial process. Positive adsorption of the solubilizing agent at the interface separating the aqueous solubilizing agent solution and a relatively water-insoluble fatty compound will be considered a prerequisite for solubilization.

Energy considerations indicate that the adsorbed surface-active compound will be oriented at the interface with the hydrophilic portion of the molecule toward the aqueous phase. Since the sparely soluble substrates are commonly hydrocarbon in nature, the hydrophobic tail of the adsorbed molecule may be considered to be dissolved in the substrate. Actually, a more extensive partitioning of the surface-active material may take place from the aqueous phase to the substrate, particularly if the substrate is a polar liquid. The interfacial region might best be considered as a special type of solution of the surface-active compound in the sparely soluble substrate, at least for the period immediately following the contact of the two phases.

Compounds which function as solubilizing agents exist largely as aggregates in aqueous solution. The aggregated state must then be the most stable configuration for the system under the prevailing conditions. If the reasonable assumption is made that a distribution of aggregate sizes exists in solution, some molecularly dispersed material as well as some very small aggregates must be present. These latter components, because of the relatively large hydrocarbon surface in contact with the water, would most likely be adsorbed at the interface. In the interface, with the hydrocarbon tail in contact with the hydrocarbon substrate, a reduction in the free energy of the molecularly dispersed component of the aqueous phase would be expected, i.e., through adsorption, a more stable state is attained.

Once adsorbed at the interface, however, these adsorbed components assumed a structure similar to that which exists in the aggregates in solution, the only difference being that at the interface the adsorbed material

is associated with the substrate. Because of the highly oriented character of the molecules in the interface, a kind of complex may be assumed to be formed by the adsorbed compound and the material of which the substrate is comprised. When some number, β, of the surface-active agent molecules become associated with a given molecule of the substrate, the over-all properties of the complex of $(\beta+1)$ molecules may be such as to allow the whole of the complex to enter the aqueous phase. To have this occur, the aggregate would have to be stable in the aqueous phase. Solubilization, then, will be considered as resulting from the formation of a soluble complex at the interface, the complex being formed through adsorption (and partitioning) of the solubilizing agent from the aqueous phase.

Physically, the situation is almost identical with that of a ternary system of two immiscible liquids and a third compound which is soluble to some extent in both liquids. The system is complicated by the fact that the third component exists in an associated state in at least one of the liquid phases. With the ordinary ternary system (no association), an area of concentration exists over which the system is homogeneous, i.e., the three components are miscible. On further addition of one of the liquid compounds, a phase separation is effected. Two phases are formed, each of which contains all three components of the system.

In solubilization, the assumption has been made that each mole of the solubilizate must be associated with at least β moles of the solubilizing agent. When the over-all composition of the system is such that fewer than β moles of solubilizing agent are present per mole of the solubilizate, a phase separation would be expected. A phase separation has been observed experimentally in these systems.

No attempt will be made to define the system over the heterogeneous region. At the phase boundary, however, some characterization of the system will be attempted in the subsequent section.

The over-all behavior of the three component systems of interest might be expected to vary considerably. When the value β required for solubilization is large, very little solubilization might be expected, particularly in solutions in which the concentrations of aggregates of size β and larger are negligible. If the solubilizing agent is only sparely soluble in the solubilizate (or vice versa), the probability of saturating the aggregated phase appears unlikely. Solubilization, in this case, would be effected at the interface proper and an equilibrium would be attained between the pure solubilizate and the aqueous phase. The solubilization of nonpolar hydrocarbons might well be included in systems of this type.

Microscopic observations of the interface separating a fatty substance and a solution of a surface-active agent lend some support to the postulated mechanism. Descriptions of what occurs at the interface all follow a similar pattern (51, 52). The interface immediately after being formed becomes ragged and uneven. Cavities appear to be formed and small droplets of the fatty material are dislodged and enter the aqueous phase. Frequently, hair-like filaments appear to grow from the surface of the fatty compound (called myelin figures) and apparently disappear in the aqueous solution. Stevenson (52) has studied the behavior of a number of pure fatty compounds in the presence of various aqueous detergent solutions and found that a large number of the investigated combinations respond in one of the described manners.

QUANTITATIVE TREATMENT

In the preceeding discussion, solubilization was described as resulting from the formation of an interfacial complex. Once some number, β, of the solubilization agent molecules became associated with a molecule of the sparely soluble compound, the adsorption complex assumed over-all hydrophilic properties and was rendered "soluble".

The assumption may be made that at the solubilization limit, the aqueous phase is saturated with the solubilizate. In the aqueous phase, then, each molecule of the solubilizate must be associated with at least β moles of the solubilizing agent. Assuming that a distribution of discrete aggregates are present in solution, only those aggregates of size equal to or greater than β will participate directly in the solubilization of a given compound. Knowing the aggregate distribution function and the value of β, the possibility exists that the solubilization limit for a given system may be estimated.

Unfortunately, very little is known regarding the size distribution function of the aggregates in solution. Initially, the assumption might be made that this distribution could be experimentally determined in much the same manner as the chain length distribution is determined for polymer solutions. Because of the reversible nature of the aggregation involved, these techniques do not appear applicable. Under these circumstances, recourse must be made to some indirect approach for the characterization of the distribution function.

Mention has already been made in the DEVELOPMENT OF BACKGROUND section that the statistical theories of solutions have been applied to solutions of "associated" liquids. Meyer and van der Wyk (29) have utilized this approach in defining a size distribution function for solutions of aggregation colloids. Although the validity of this treatment has never been experimentally established, this means of attacking the problem appears to be the best available, particularly because the essential results are not biased by numerous initial assumptions.

In deriving this distribution function, the aggregation is assumed to proceed in the following manner:

$$A + A \rightleftharpoons A_2 \qquad K_1 = \text{Equilibrium constant}$$
$$A_2 + A \rightleftharpoons A_3 \qquad K_2 \qquad " \qquad "$$
$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$
$$A_v + A \rightleftharpoons A_{v+1} \qquad K_v \qquad " \qquad "$$

By assuming that the free energy decrease per molecule entering an aggregate is independent of the aggregate size, the equilibrium constants for each step become identical, i.e., $K_1 = K_2 = K_v$.

The equilibrium may then be expressed as:

$$\frac{n_{v+2}}{n_1 \circ n_{v+1}} = \frac{n_{v+1}}{n_1 \circ n_v} = \frac{n_v}{n_1 \circ n_{v-1}} = \cdots\cdots = \frac{n_3}{n_1 \circ n_2} = \frac{n_2}{n_1^2} = \underline{K} \qquad (1)$$

The equilibrium mixture is described here in terms of the moles of aggregate of a fixed size, i.e., n_{v+2} denotes the number of moles of size v+2.

Equation (1) may be rewritten:

$$n_2 = n_1^2 \underline{K}$$

$$n_3 = n_1^3 \underline{K}^2$$

$$n_4 = n_1^4 \underline{K}^3 \qquad (2)$$

$$\vdots$$

$$n_v = n_1^v \underline{K}^{v-1}$$

The total concentration of the solubilizing agent in solution, $\underline{S}_M$, in terms of the monomer, may be obtained from the summation:

$$\underline{S}_M = \sum_{v=1}^{v=\infty} v n_v = \sum_{v=1}^{v=\infty} v n_1^v \underline{K}^{v-1} = \frac{n_1}{(1-n_1\underline{K})^2} \qquad (3)$$

From (3), the concentration of monomer may be obtained in terms of $\underline{K}$ and $\underline{S}_M$:

$$n_1 = \frac{2\,\underline{K}\underline{S}_M + 1 - \sqrt{4\underline{K}\underline{S}_M + 1}}{2\underline{K}^2 \underline{S}_M} \qquad (4)$$

By means of Equations (4) and (2), the concentrations of each species in solution may be determined if a value for $\underline{K}$ is given.

The assumption has been made that β moles of the solubilizing agent are necessary to solubilize a single mole of the solubilizate. As a corollary to this proposition, aggregates made up of fewer than β molecules must be considered inactive in solubilization. An effective concentration of the solubilizing agent in solution may then be calculated by subtracting the concentration of aggregates smaller than β from the total concentration. Certain decisions must, however, be made before this is done.

According to the mechanism proposed, the aggregates in solution cannot be regarded as being fixed entities. More properly, the association must be viewed as being dynamic. The molecules of the complex formed at the interface, once in the aqueous phase, must be considered as participating in the association process if the equilibrium relation governing aggregation is to remain undisturbed. For the solubilized molecule to remain in "solution", β molecules of the solubilizing agent must be dynamically associated with each solubilizate molecule. Utilizing the distribution function just discussed, an estimate may be made of the fraction of the total associating material which can be assumed to be associated in aggregates of size smaller than β. That fraction of the solubilizing agent which is capable of forming aggregates of size greater than β will be considered the effective concentration. The effective fraction of the solubilizing agent will be assumed capable of solubilizing one molecule of the solubilizate per β molecules of the solubilizing agent.

Using these assumptions as a basis for calculation, an effective concentration, $\underline{S}_E$, for solubilization can be defined:

$$\underline{S}_E = \underline{S}_M - \sum_{v=1}^{v=\beta} v n_1^v \underline{K}^{v-1} \qquad (5)$$

From (5), the quantity of material solubilized, $\underline{R}$, per liter of solution of stoichiometric concentration $\underline{S}_M$ becomes:

$$\frac{1}{\beta}\left(\underline{S}_M - \sum_{v=1}^{v=\beta} v n_1^v \underline{K}^{v-1}\right) = \underline{R} \qquad (6)$$

Because of the discontinuous nature of the distribution function, the term in parentheses in (6) must be considered to be only a good estimate of

the effective concentration (i.e., only integral values of β may be used in evaluating the summation term). Since the association process has been considered from the dynamic point of view, no a priori reasons exist for restricting the actual values of β to integral values. The values of β to be calculated later will be average values and should fall within the range (of values of β) dictated by the value of β used in evaluating the summation term. The summation term may be evaluated for integral values of β to give the following equations:

$\beta \geq 1<2$

$$\frac{1}{\beta}\left(S_M - \frac{1}{K} + \frac{1}{2K^2 S_M}\left[\sqrt{4KS_M + 1} - 1\right]\right) = R \qquad (7)$$

$\beta \geq 2<3$

$$\frac{1}{\beta}\left(S_M - \frac{3}{K} + \frac{1}{2K^2 S_M}\left[5\sqrt{4KS_M+1} - 9\right] + \frac{1}{K^3 S_M^2}\left[\sqrt{4KS_M+1} - 1\right]\right) = R \qquad (8)$$

$\beta \geq 3<4$

$$\frac{1}{\beta}\left(S_M - \frac{6}{K} + \frac{1}{K^2 S_M}\left[7\sqrt{4KS_M+1} - 18\right] + \frac{1}{K^3 S_M^2}\left[7\sqrt{4KS_M+1} - 10\right]\right) = R \qquad (9)$$

$\beta \geq 4<5$

$$\frac{1}{\beta}\left(S_M - \frac{10}{K} + \frac{1}{K^2 S_M}\left[15\sqrt{4KS_M+1} - 50\right] + \frac{1}{K^3 S_M^2}\left[27\sqrt{4KS_M+1} - 50\right]\right) = R \qquad (10)$$

Equations (9) and (10) are approximations, terms containing K to powers larger than 3 being dropped. Each of these expressions contains two constants, β and K. Obviously, these equations could be tested by substituting values for β and K and comparing calculated values of R with the experimental values. No means exists, however, for independently evaluating β and K.

An alternative procedure must then be introduced for testing the derived expressions. Rather than using values of $\underline{K}$ and β to calculate $\underline{R}$, the experimentally determined values of $\underline{R}$ may be utilized in obtaining estimates of $\underline{K}$ and β (sample calculation--Appendix III).

For these calculations to be made, some estimate must be made of β. This is necessary in selecting the correct equation (7-10) for representing a given set of data. Estimates of β can be readily obtained from the experimental data by plotting the moles of solubilizing agent required to solubilize a mole of the solubilizate as a function of the solubilizing agent concentration. As the concentration is increased, the mole per mole ratio tends to approach a limit, this limit being an estimate of β. The correct equation may be selected on the basis of the β value determined in this manner, each of the listed equations covering a range of β values. Using the estimated value of β and the experimental values of $\underline{R}$, values for $\underline{K}$ and β can be determined by a successive approximation technique. These constants possibly could be determined by a least squares procedure but this requires an equally laborious trial and error calculation. Actually, the described solution is only approximate because the size distribution function has been assumed to be continuous. In deriving the equations, the discontinuous nature of the distribution was considered. As a result of this approximation, the calculated quantity β may assume other than integral values. This does not, however, appear to be a serious objection to the treatment presented.

When the values of β and $\underline{K}$ are obtained, the goodness of fit of the resulting expression can be determined by comparing calculated values of $\underline{R}$

with the experimental values. Since the assumption has been made that the distribution character is unchanged by the presence of the solubilizate, identical values of K should be obtained under similar conditions employing a given solubilizing agent solution but using different solubilizates. The values of β would be expected to vary for different solubilizates.

The data obtained from the series of experiments using the nonionic solubilizing agent will be examined initially. These data should be more amenable to treatment than those obtained from the experiments with the ionic agent because of the greater probability of interactions due to the presence of the ionic constituents in the latter.

Application of Theory to Solubilization Experiments with the Nonionic Solubilizing Agent

The data obtained from the series of experiments in which polyethenoxy tetradecyl ether was used as the solubilizing agent have been re-examined according to the theory outlined. The experimental results have been previously presented in Figure 7.

Estimates of β and K were made by substituting corresponding values of S_M and R into Equation (7) and solving the resulting expressions by trial and error. The values obtained were:

Solubilizate	K_o'' liter-mole^{-1}	moles solubilizing agent / mole solubilizate
Oleic acid	1400	1.62
n-Octadecanol	1400	1.65

By substituting these values into Equation (7), an estimate of the goodness of fit of the derived expression can be obtained by comparing the calculated values with those obtained from the experimental curve. The values of $\underline{R}_{Calc.}$ and $\underline{R}_{Exp.}$ (read from experimental curve) are listed in Table III.

TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF $\underline{R}$

	n-Octadecanol		Oleic Acid	
S_M	$\underline{R}_{Calc.}$	$\underline{R}_{Exp.}$	$\underline{R}_{Calc.}$	$\underline{R}_{Exp.}$
.001	0.000409	0.000409	0.000413	0.000413
.005	0.00272	0.00272	0.00277	0.00282
.010	0.00572	0.00572	0.00585	0.00580
.015	0.00870	0.00867	0.00885	0.00881
.020	0.0107	0.0108	0.0119	0.0120

From this tabulation, the conclusion may be drawn that the derived expression [i.e., Equation (7)] does fit reasonably well the experimental data over the investigated range. The correspondence of the values of the association constant appeared as was anticipated. The β values indicate that oleic acid would be solubilized to a slightly greater extent than n-octadecanol.

Reference has previously been made regarding the observation that solutions of solubilizing agents below a certain critical concentration are unable to effect any measurable solubilization. In general, the concentration at which aggregation first is observed to take place and the

concentration at which solubilization first is detected are considered one and the same. According to the present treatment, the concentration at which solubilization is first observed should be the concentration at which the mean aggregate size becomes larger than the value β for the particular compound being solubilized. Since measurements of the colligative properties of the solutions do indicate that the onset of appreciable association takes place over a rather narrow concentration range, the two concentrations in question may appear to be the same, but this is not required. This difference should be easily detected when β is large.

By extrapolating the curves of Figure 7 to $\underline{R} = 0$, values of about 0.00015 and 0.00019M are obtained as the concentrations at which oleic acid and n-octadecanol are first solubilized.

Application of Theory to Solubilization Experiments Using Sodium Tetradecyl Sulfate as the Solubilizing Agent

The data obtained from the series of experiments using sodium tetradecyl sulfate as the solubilizing agent have been presented in Figures 9-12 and discussed qualitatively. The derived expressions, by inspection, will not represent the behavior of either system beyond the concentration at which the maximums were attained in Figures 10 and 12. In the previous interpretation given these data, the form of these solubilization limit-concentration curves was assumed to be the result of interactions between the solubilizate and the cations supplied by the dissociation of the solubilizing agent. The adsorption of sodium ions by the aggregates containing solubilizate would be expected to alter the equilibrium which normally would exist between the

aggregates and the cations. Aside from the dehydration effects which the adsorption of the cation might induce, changes in the aggregate distribution might also be effected.

In the first analysis, the quantity and polarity of the solubilizate would be factors controlling the adsorption of gegenions by the aggregates. In aggregates containing a high ratio of solubilizing agent to solubilizate, the secondary gegenion adsorption might not be important. In dilute solutions, regardless of the nature and amount of the solubilizate, the additional gegenion adsorption would be of a magnitude that would have little effect on the over-all behavior of the system.

Thus, the possibility exists that the data obtained over the very dilute concentration region might satisfactorily be described by the derived expressions. In Figure 13, the data obtained over the dilute region for the experiments in which n-octadecanol was the solubilizate have been plotted on an expanded scale (many of the plotted values were obtained by interpolation of the smooth curves shown in Figure 10). The same procedure has been followed in preparing Figure 14 for oleic acid in solutions of the same solubilizing agent. In both cases, these plots suggest that the data might be described by the derived equations.

Equations of the forms (8-10) were found to fit the experimental data reasonably well (See Table IV). The values of the constants determined at the different conditions were:

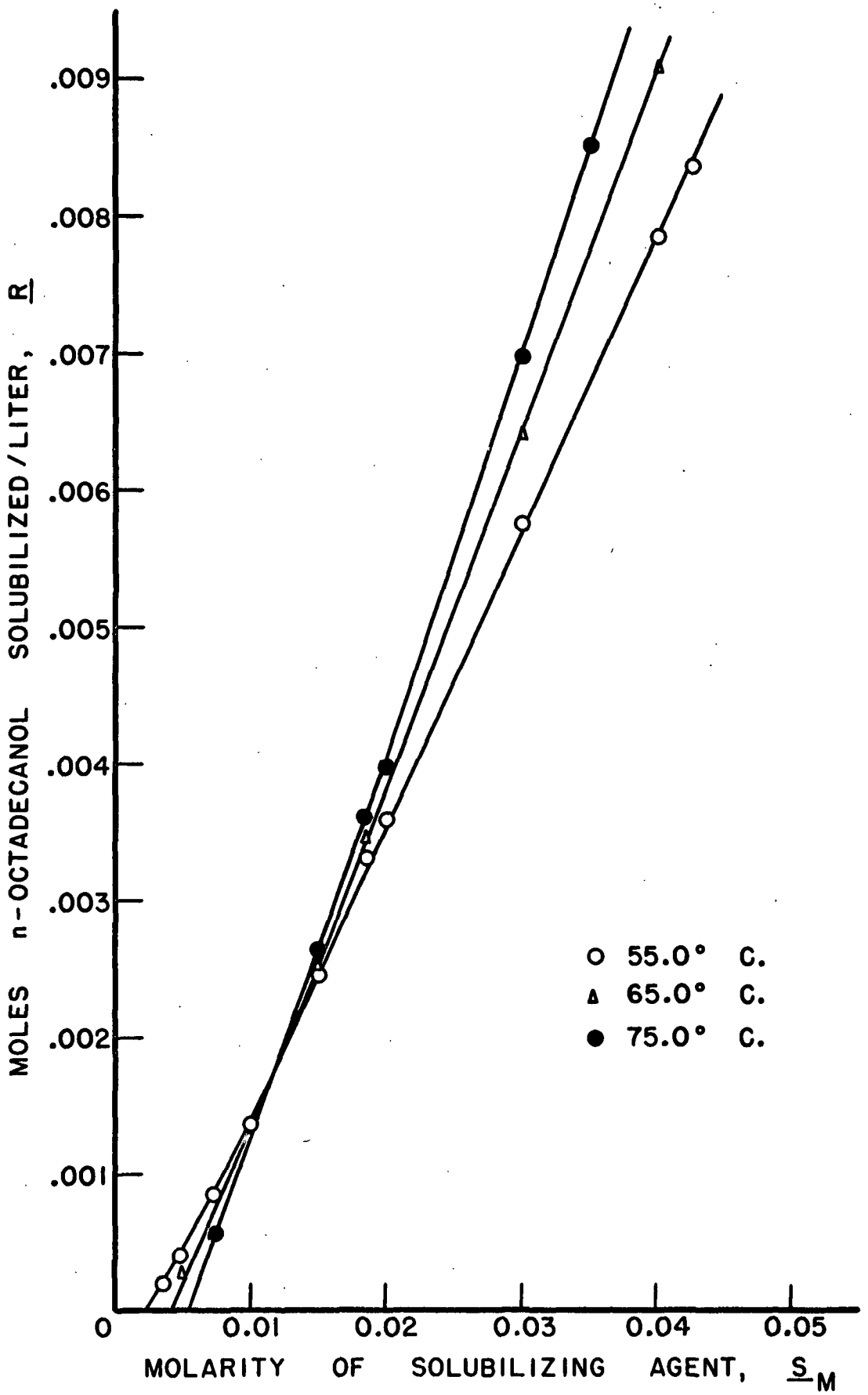


Figure 13. The Solubilization Limits of n-Octadecanol in Dilute Solutions of Sodium Tetradecyl Sulfate

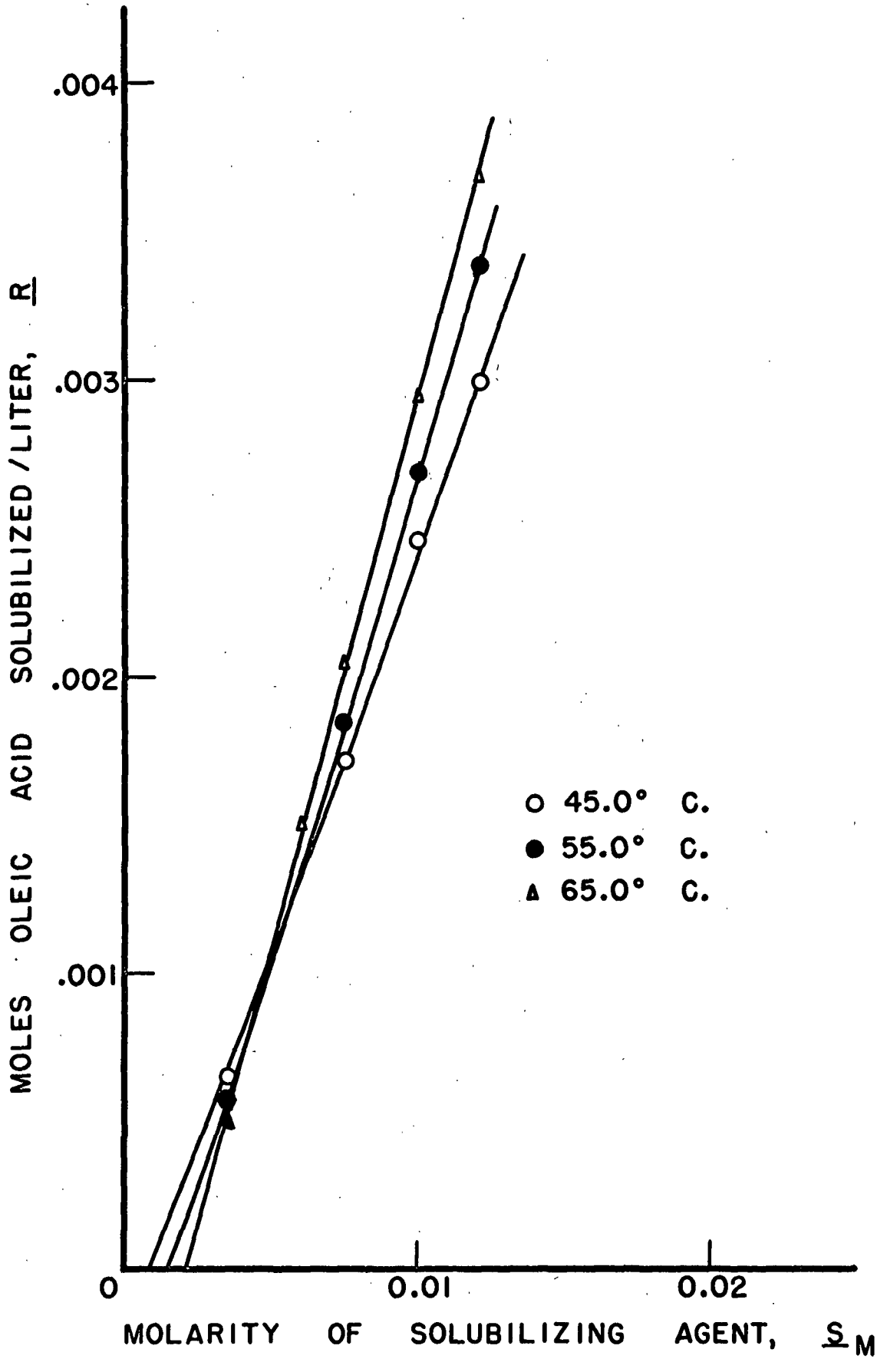


Figure 14. The Solubilization of Oleic Acid by Dilute Solutions of Sodium Tetradecyl Sulfate

Solubilizate	Temp., °C.	K, liters/mole	β, Moles/Mole
n-Octadecanol	55.0	1800	4.55
	65.0	600	3.90
	75.0	315	3.05
Oleic Acid	45.0	3300	3.62
	55.0	1800	3.05
	65.0	570	2.46

These derived data tend to support in part the quantitative interpretation previously presented. Values of K are observed to decrease with increasing temperature. This indicates that the aggregation tendency is adversely influenced by higher temperatures. At the same time, however, the solubilizing agent demand per molecule of the solubilizate (β) is decreased as the temperature is increased, i.e., the efficiency per molecule is greater at elevated temperatures. The increased efficiency of the solubilizing agent could be attributed to increased hydration of the hydrophilic group.

At a given temperature, corresponding values of the equilibrium constant were obtained, indicating that the solubilizate does not appreciably influence the over-all aggregation equilibrium. At any given temperature, the solubilizing agent demand of oleic acid is less than that required by n-octadecanol. The paucity of data do not permit a detailed study of the factors responsible for the difference in solubilization behavior of these two compounds, but the values of β should be useful in studying solubilizate-solubilizing agent relationships.

TABLE IV

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF R

Solubilizate	Temp., °C.	S_M	$R_{calc.}$	$R_{exp.}$
oleic acid	45.0	0.0035	0.00081	0.00070
		0.0050	0.00107	0.00106
		0.0100	0.00243	0.00242
		0.0125	0.00310	0.00311
oleic acid	55.0	0.0035	0.00069	0.00060
		0.0050	0.00105	0.00105
		0.0100	0.00262	0.00265
		0.0125	0.00344	0.00351
oleic acid	65.0	0.0035	0.00071	0.00060
		0.0050	0.00118	0.00112
		0.0100	0.00297	0.00296
		0.0125	0.00389	0.00386
n-octadecanol	55.0	0.0100	0.00139	0.00140
		0.0200	0.00365	0.00355
		0.0300	0.00580	0.00575
		0.0400	0.00802	0.00792
n-octadecanol	65.0	0.0100	0.00150	0.00135
		0.0200	0.00379	0.00378
		0.0300	0.00620	0.00645
		0.0400	0.00865	0.00910
n-octadecanol	75.0	0.0100	0.00130	0.00130
		0.0200	0.00397	0.00400
		0.0300	0.00686	0.00695
		0.0400	0.00982	0.00992

In examining the derived information, the observation is made that the calculated equilibrium constants for the ionic solubilizing agent are dependent on temperature. Ordinarily this dependence would be expected to assume the form:

$$\underline{R}_g\left(\frac{\partial \ln \underline{K}}{\partial\left(\frac{1}{\underline{T}}\right)}\right)_p = -\Delta H^\circ, \text{ where} \qquad (11)$$

$\underline{R}_g$ = gas constant;

$\underline{K}$ = equilibrium constant;

$\underline{T}$ = absolute temperature; and

ΔH° = standard heat of formation.

Having values of the equilibrium constants at different temperatures, an estimate of the standard heat of formation can be made. When log $\underline{K}$ is plotted *versus* $1/\underline{T}$, the slope of the tangent to the curve at any temperature is equal to $-\frac{\Delta H}{\underline{R}_g}$. If the heat capacities of the products and the reactants are equal, a straight line should result when the plot is prepared as described.

From the present solubilization experiments, the aggregation or equilibrium constants have been obtained at four temperatures. In Figure 15, these data have been plotted in the prescribed manner. A fifth point, obtained from data appearing in the literature (53), has been included in Figure 15 (these data are presented in APPENDIX II). The relationship between the association constant and temperature appears to be linear in the plotted variables. From the slope of this line a value of -2.1 kcal./mole has been obtained as the standard heat of formation, or in this case, the standard heat of aggregation.

Estimates of the heat of aggregation ranging from -1.5 to -5.5 kcal./mole over the temperature range 35-80°C. for sodium tetradecyl sulfate have been made by Stainsby and Alexander (54). These estimates are based on the temperature-solubility relationship and on the effect of temperature on the critical micelle concentration. Goddard, Hoeve, and Benson (55) have devised a calorimetric technique for experimentally determining heats of aggregation but results were reported only for lower alkyl sulfates.

The value of the heat of aggregation obtained in this work appears reasonable, being of the order of magnitude expected for a process involving secondary valence forces.

Re-examination of the Concept of the Critical Concentration for Micelle Formation

In the past, workers in the field of solubilization have maintained that no solubilization may be effected below that concentration at which the colligative properties indicate appreciable association of the aqueous system being studied. The data obtained in the present work indicate that the concept of a fixed critical concentration may be erroneous.

In terms of the foregoing presentation, the concentration at which solubilization is first detected appears to be related to the parameters involved in a particular system. This relationship may be established if the assumption is made that no solubilization is possible at concentrations of the solubilizing agent below which the mean degree of aggregation is less than the calculated value of β. Using the given distribution function, various average degrees of aggregation may be calculated. The weight average

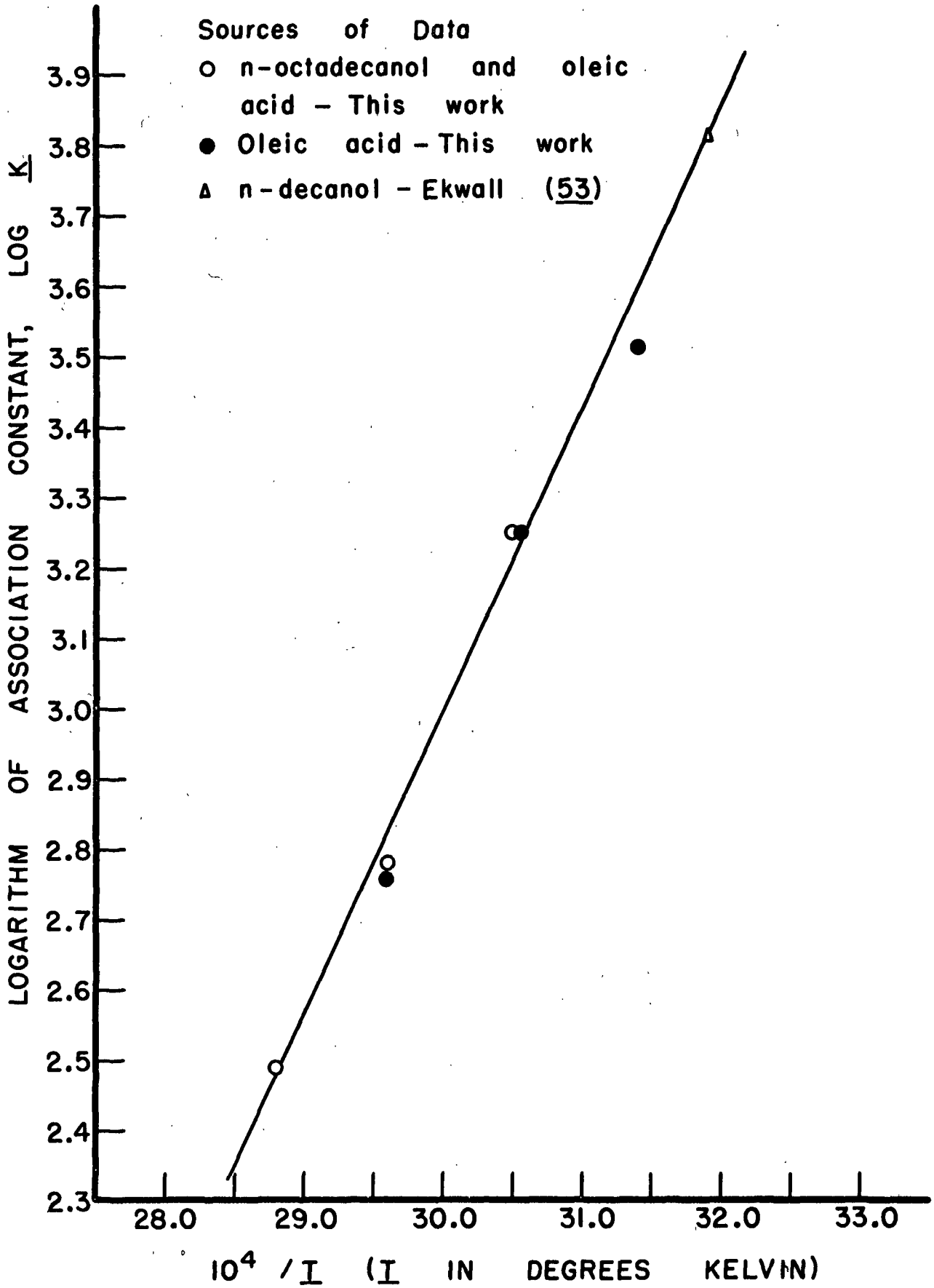


Figure 15. Correlation of Association Constant Data-Aqueous Solutions of Sodium Tetradecyl Sulfate

degree of aggregation has been found to give reasonably satisfactory results. (If any single molecule of the solubilizing agent is selected at random from the aqueous solution, it may be shown that the weight average degree of aggregation represents the statistically expected size of the aggregate of which the selected molecule is a part.)

The weight average degree of aggregation $\bar{v}_w$ may be obtained from the following equation:

$$\bar{v}_w = \frac{\sum_{v=1}^{v=\infty} v^2 n_v}{\sum_{v=1}^{v=\infty} v n_v}, \qquad (12)$$

the terms being the same as those used in Equations (1-5). By substituting the equivalent expression from Equations (2) and (4) into this expression and summing, the following expression for $\bar{v}_w$ is obtained:

$$\bar{v}_w = \sqrt{4\underline{K}\underline{S}_M + 1}. \qquad (13)$$

According to the previous assumption, $\bar{v}_w = \beta$ when $\underline{R}=0$. The appropriate value of $\underline{S}_M$ to substitute in (13) should be the value of $\underline{S}_M$ obtained by extrapolating the $\underline{R}$-$\underline{S}_M$ function to $\underline{R}=0$.

Having estimates of β and $\underline{K}$, Equation (13) may be solved for $\underline{S}_M$ and the calculated values compared with the extrapolated values. The equation to be used becomes:

$$\frac{\beta^2 - 1}{4\underline{K}} = \underline{S}_M. \qquad (14)$$

The calculated and the extrapolated values of S_M are listed in Table V.

TABLE V

COMPARISON OF EXTRAPOLATED AND CALCULATED VALUES OF S_M

System	S_M Calculated	S_M By Extrapolation
Polyether-oleic acid	0.00029	0.00015
Polyether- n-octadecanol	0.00031	0.00019
Sodium tetradecyl sulfate-oleic acid		
45°C.	0.00087	0.0008
55°C.	0.0010	0.0013
65°C.	0.0017	0.0021
Sodium tetradecyl sulfate- n-octadecanol		
55°C.	0.0027	0.0025
65°C.	0.0057	0.0042
75°C.	0.0068	0.0055

All factors considered, the agreement between the extrapolated and the calculated values appears to be reasonable.

THE SOLUBILIZATION OF SOLIDS BY AQUEOUS POLYETHENOXY TETRADECYL ETHER SOLUTIONS

In studying the ordinary solubility of a specific solute in a given solvent, the observation is made that the solubility-temperature relationship exhibits an abrupt break or transition at the melting point of the solute. A given solute is almost always more soluble in the selected solvent

at temperatures above the fusion point of the solute. The heat of fusion of the solid may be considered a barrier to the dissolution of the solid. Because of the similarities between solubilization and solution, a similar relationship between the solubilization limit and temperature might be suspected to exist.

Solid solubilizates have been employed in numerous solubilization experiments, but the temperature-solubilization limit relationship has not been defined satisfactorily. In most of these experiments low molecular weight oil-soluble organic dyestuffs have been the most common solubilizates utilized. In almost all of these experiments ionic solubilizing agents have been used. The observation has been made in this work that the solvent properties of the ionic compounds are temperature dependent. In these experiments, then, some confounding of the variables might be suspected.

The nonionic solubilizing agent used in the previous experiments with liquid solubilizates appeared to be an ideal material for conducting solubilization experiments with solids. Temperature had little effect on the solvent properties of these solutions. Using a fixed concentration of the solubilizing agent for all experiments, the assumption might be made that variations in the temperature-solubilization limit relationship could be attributed to the solubilizate-solubilizing agent interactions rather than to temperature-induced changes in the solvent properties of the solubilizing agent solution.

Attempts were made to solubilize a total of five compounds. Arbitrarily, a 0.00915M (0.810%) solution of polyethenoxy tetradecyl ether was utilized in

this investigation. Temperature was varied over a range below the melting temperature of the particular solid being studied.

Stearic acid, n-octadecanol, and abietic acid were solubilized to an appreciable extent under the conditions employed. The results of this study are presented in Figure 16 (data—Table VI). Neither β-sitosterol nor trimyristin could be solubilized to any measurable extent over the temperature range explored, the upper limits being 50°C. for trimyristin and 82°C. for β-sitosterol.

The solubilization experiments were conducted according to the method outlined in EXPERIMENTAL PROCEDURES. Free abietic acid appeared in that system when the solubilization limit was exceeded, indicating that the solubilized phase can exist in equilibrium with solid abietic acid. When stearic acid and n-octadecanol were utilized as solubilizates, a somewhat different situation was obtained. When the solubilization limit was exceeded with either of these compounds, the system assumed a smectic appearance. When either compound was allowed to stand in contact with the aqueous solubilizing agent solution at room temperature, the smectic phase was spontaneously formed. This condition could also be attained when systems containing these compounds in a solubilized state (at temperatures above the melting point of the solid) were cooled to temperatures below the melting point of the compound being investigated. These observations could indicate that the solubilized phase exists, over the region explored, in equilibrium with a liquid-crystalline phase, i.e., a liquid-state equivalent to a mixed crystal or solid solution.

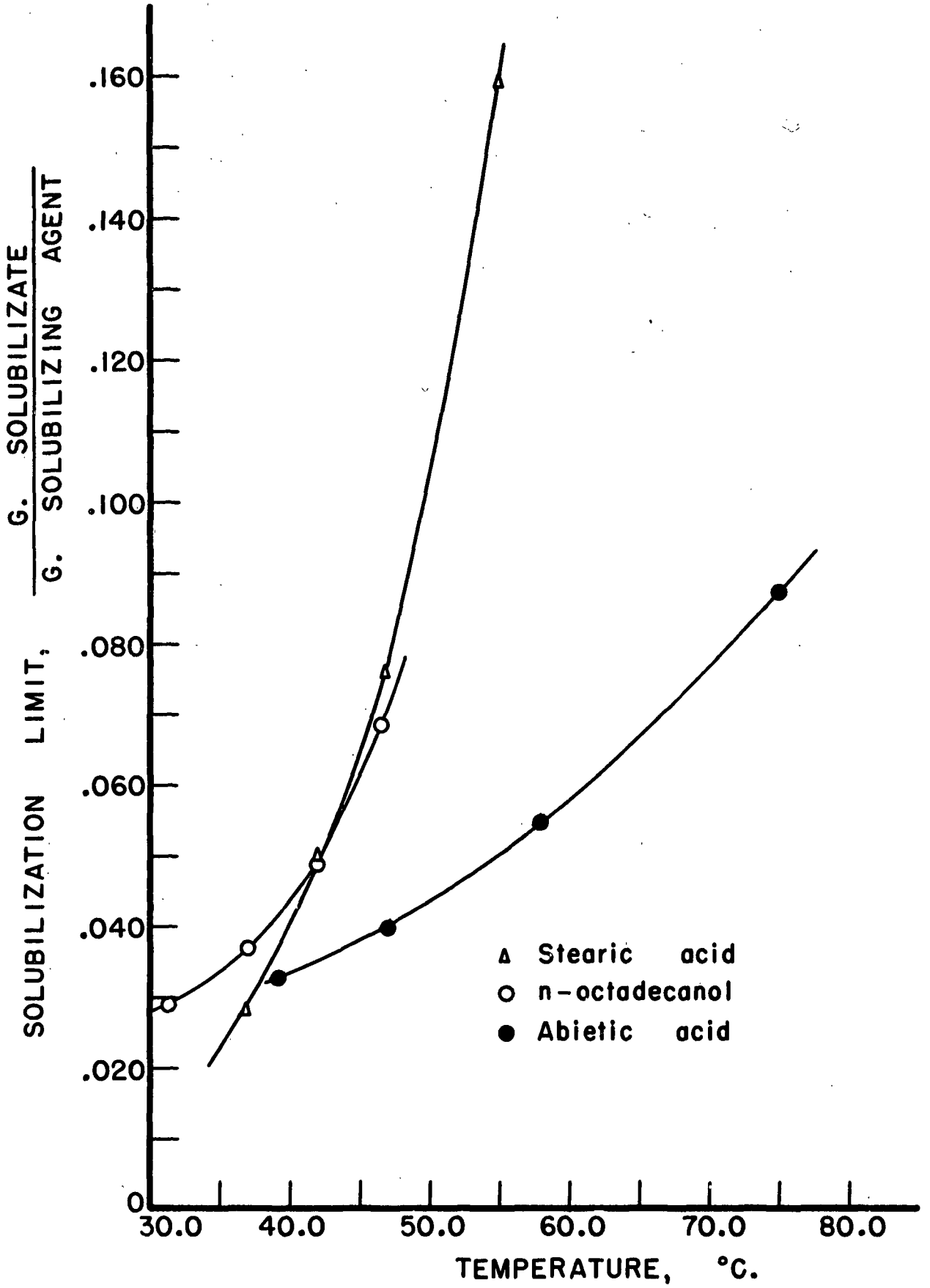


Figure 16. Effect of Temperature on the Solubilization of Solids by Aqueous Polyethenoxy Tetradecyl Ether Solutions

TABLE VI

SOLUBILIZATION LIMITS OF SOLIDS IN 0.8100% POLYETHENOXY TETRADECYL ETHER AT TEMPERATURES BELOW THE MELTING POINTS

Solubilizate	Temp., °C.	Solubilization Limit	
		g. solubilizing / g. solubilizing agent	Moles-solubilizate / Moles solubilizing agent
n-octadecanol	31.2	0.029	0.095
	37.0	0.037	0.121
	42.0	0.049	0.160
	46.5	0.069	0.226
stearic acid	36.8	0.028	0.087
	42.0	0.050	0.156
	46.8	0.076	0.237
	54.8	0.160	0.498
abietic acid	39.2	0.033	0.097
	47.0	0.040	0.117
	58.0	0.055	0.161
	75.0	0.088	0.219

The phase which separates when the solubilization limit is reached at temperatures above the melting temperature of n-octadecanol is an amorphous liquid. For this solubilizate, the assumption may be made that a transition temperature exists, presumably the melting temperature, below which this material is solubilized to a lesser extent than above the transition temperature. A similar situation would be expected for stearic acid.

In the preceding study of the solubilization of liquids, some mechanistic aspects of the solubilization process were considered. No a priori reasons exist, however, for restricting the proposed mechanism to systems in which the solubilizate is liquid.

Adsorption of the solubilizing agent at the solid-liquid interface will be considered essential for solubilization. At the interface, a complex will be formed as with liquid solubilizates. Since all adsorption processes are exothermic, the solid in the immediate vicinity of the interface might actually be molten momentarily if the heat of fusion of the solid and the heat of adsorption are of the same magnitude. At temperatures below the transition temperature, however, the formed complex would not be as stable in the aqueous phase as when the solubilizate is liquid. This instability would be reflected in smaller amounts of the solid being solubilized at temperatures below the transition temperature.

If, due to the heat liberated during the adsorption of the solubilizing agent, nonequilibrium conditions prevail at the interface, the aqueous phase might become supersaturated with respect to the adsorption complex. The excess complex in the aqueous phase would be decomposed, the solubilizate

presumedly tending to recrystallize into the normal crystalline lattice. The solid surfaces present, however, are protected by an adsorbed layer of the solubilizing agent and hence are not available as crystallization sites. The molecules of solubilizate are closely associated with molecules of the solubilizing agent, reducing the probability of nuclei forming in suspension. To assume a more stable state, some mixture of the solubilizing agent and the solubilizate would be thrown out of solution, i.e., a metastable phase was formed. Conceivably, the smectic condition noted in two of the systems could be the metastable state assumed. If equilibrium conditions prevailed during the entire process, solid solubilizate would exist in equilibrium with the solubilized phase when the solubilization limit is exceeded.

In the solubilization of abietic acid, the pure solid existed in equilibrium with the solubilized phase when the solubilization limit was exceeded. The possibility exists that the data obtained using abietic acid as a solubilizate might be amenable to further analysis. At equilibrium, the free energy of the solid, $\underline{F}_2^S$, must necessarily equal the partial molal free energy of the solubilizate in the aqueous phase, $\overline{\underline{F}}_2^S$. Since the standard state of one of the participating phases is known (the solid), some further analysis of these data seems possible.

To utilize this information, a reversible path for the solubilization process must be contrived, the separate steps of which are calculable. First, the solid must be melted to a supercooled liquid at the temperature of the experiment. This supercooled liquid is then to be mixed with the aggregated solubilizing agent, at the equilibrium concentration, i.e., the saturated concentration.

If the heat of mixing the solubilizate with the solubilizing agent is zero, the solubilization phenomenon may be treated in exactly the same manner as the dissolution of a solid to form an ideal solution.

Hildebrand (56) treats this latter case extensively, deriving the following equation to represent the behavior of these systems:

$$\log_{10} x_2 = \frac{-\Delta H_m^F}{4.58}\left(\frac{T_m - T}{T_m T}\right) \quad , \text{ where}$$

x_2 = mole fraction of the solute;

ΔH_m^F = heat of fusion at the melting point; and

T, T_m = temperature at which the measurements are made and the temperature at the melting point, respectively.

In attempting to apply this relationship to solubilization data, the mole fraction of the solubilizate must be defined. Since the aggregated solubilizing agent assumes the role of the solvent, the mole fraction term to be used in solubilization should, in the first approximation, be based on only the total moles of solubilizate and solubilizing agent in the system.

According to the equation presented, the experimental data should be rectified if log x_2 is plotted *versus* $1/T$. In Figure 17, the data for abietic acid, as well as for stearic acid and n-octadecanol, have been plotted in the designated manner. These data appear in all cases to be reasonably fitted by a relationship of the form presented. The slopes of the lines obtained may be related to the heats of fusion of the various

compounds if all of the inherent assumptions are valid. From the slopes of these lines, estimates of the heats of fusion have been made. Unfortunately, only a value of the heat of fusion of stearic acid could be obtained from the literature for comparison purposes. The values calculated (together with the known value) were:

Compound	Heat of Fusion, kcal./mole	
	Calculated	Literature
Stearic acid	15	16.4 (57), 13.5 (58)
n-Octadecanol	10	--
Abietic acid	5.1	--

The calculated value for stearic acid appears to be in agreement with the experimental values. The value for n-octadecanol appears reasonable, the experimental value for n-hexadecanol being 8.2 kcal./mole (58).

The two compounds which could not be solubilized from the solid state, β-sitosterol and trimyristin, are both relatively high molecular weight compounds. The complex formed at the interface must be completely unstable in the aqueous phase below the transition temperature.

When small quantities of either β-sitosterol or trimyristin were dissolved in oleic acid, the two-component mixtures could be completely solubilized. These experiments were not extensive enough to even permit speculation regarding the interactions in these systems. Practically, these observations indicate that compounds which are not solubilizable from the solid state can be solubilized when put in solution by a suitable solvent.

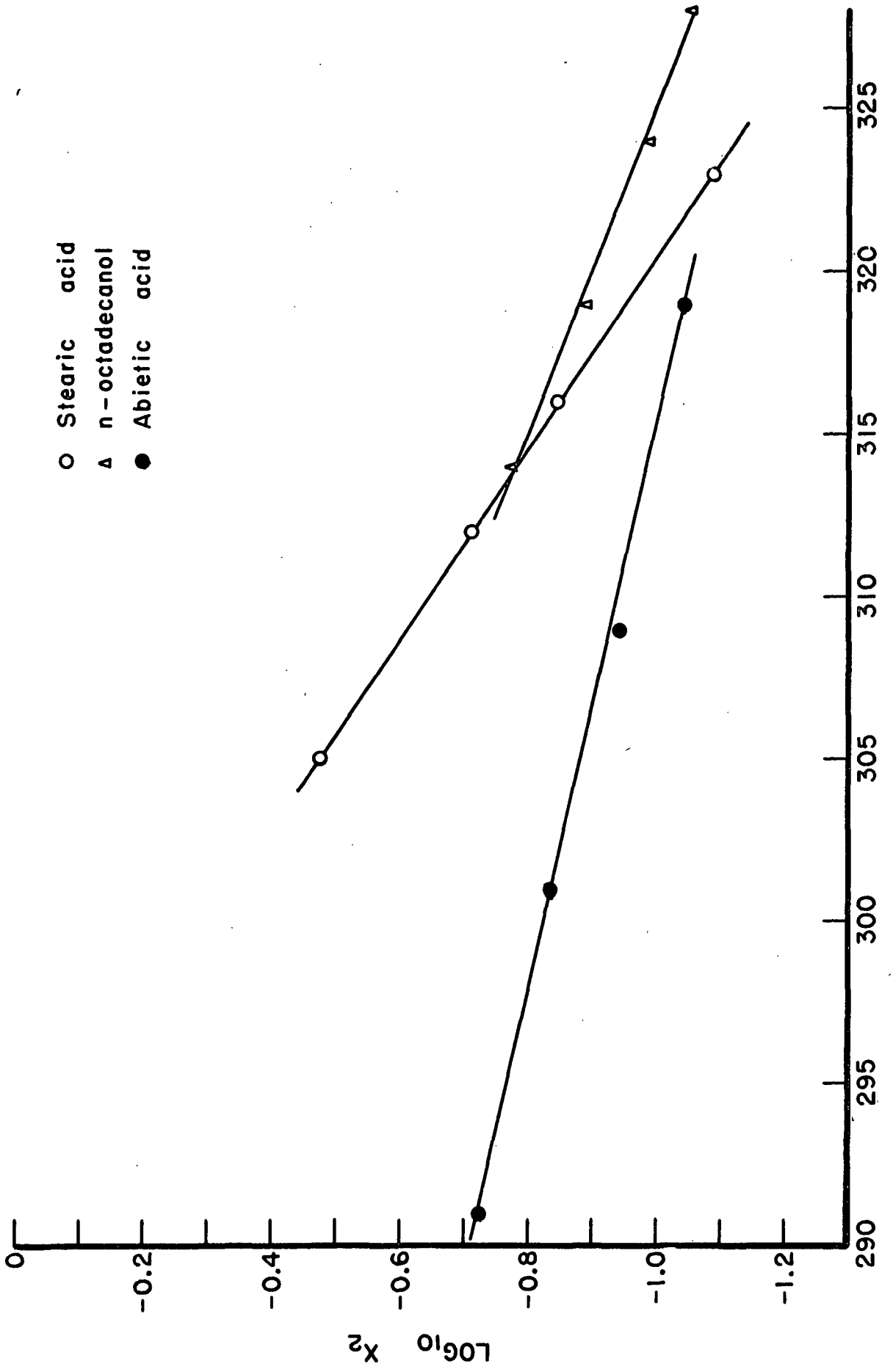


Figure 17. Solubilization of Solids by Polyethenoxy Tetradecyl Ether Solutions

An investigation of the "mixture effect" was considered to be beyond the scope of the present investigation.

THE SOLUBILIZATION OF SOLIDS BY AQUEOUS SOLUTIONS OF SODIUM TETRADECYL SULFATE

SOLUBILIZATION OF ABIETIC ACID AND β-SITOSTEROL

The solubilization limits for solid abietic acid in aqueous solutions of sodium tetradecyl sulfate were determined over a temperature range extending from 46-79°C. and over a concentration range extending from 0.00665 to 0.0425M. The data obtained from this study are presented in Figure 18. The solubilization limits for solid β-sitosterol, over a broader concentration range, are plotted in Figure 19 (Table VII).

Neither of these compounds were solubilized to any appreciable extent over the concentration and temperature ranges employed, the limits determined being at least an order of magnitude smaller than any previously measured in this investigation. In both instances, excess solubilizate in the system appeared in the free state.

The temperature-concentration dependence of the solubilization limit for both compounds appears to be of the same form as determined for the liquid oleic acid and n-octadecanol. At a fixed temperature, the solubilization limit initially increases as the concentration of the solubilizing agent solution increases. Beyond a certain concentration of the solubilizing agent solution, however, this trend is reversed. As before, this may be interpreted as resulting from an interaction between the polar groups of the solubilizate and the cations supplied by the unaggregated fraction of the system.

TABLE VII

SOLUBILIZATION LIMITS OF SOLID ABIETIC ACID, β-SITOSTEROL, AND n-OCTADECANOL IN AQUEOUS SOLUTIONS OF SODIUM TETRADECYL SULFATE

Molarity	Solubilizate	Temp., °C.	Solubilization Limit g. solubilizate / g. solubilizing agent
0.00665	abietic acid	68.7	0.0031
0.0186		68.7	0.0051
0.0339		68.7	0.0045
0.0425		68.7	0.0040
0.00665		55.0	0.0000
0.0186		55.0	0.0033
0.0339		55.0	0.0025
0.0425		55.0	0.0016
0.0186		46.0	0.0025
0.0339		46.0	0.0014
0.0425		46.0	0.0009
0.00665		78.0	0.0038
0.0186		78.8	0.0067
0.0339		77.0	0.0060
0.0425		78.8	0.0051
0.0339	β-sitosterol	54.0	0.0018
0.0639		54.0	0.0025
0.129		54.0	0.0016
0.0113		66.1	0.0007
0.0186		66.1	0.0015
0.0339		66.1	0.0025
0.0639		66.1	0.0041
0.129		66.1	0.0022
0.0186		78.0	0.0018
0.0339		78.0	0.0033
0.0639		78.0	0.0050
0.129		78.0	0.0036

TABLE VII (Continued)

SOLUBILIZATION LIMITS OF n-OCTADECANOL IN 0.121M SODIUM TETRADECYL SULFATE

Temp., °C.	g. n-octadecanol / g. solubilizing agent
38.0	0.0219
43.0	0.0516
48.5	0.118
51.5	0.174
56.0	0.179
66.0	0.191
69.0	0.195
78.0	0.204

At a fixed concentration, the solubilization limits increased with temperature. In Figure 20, the data for abietic acid have been replotted to show this trend more clearly. These data were fitted only approximately by the $\log_{10} x_2$ *versus* $1/T$ relationship used to fit the data from the experiments with the nonionic solubilizing agent.

SOLUBILIZATION OF *n*-OCTADECANOL

A limited study of the solubilization of *n*-octadecanol in a 0.121*M* sodium tetradecyl sulfate solution was made to determine the behavior of the system in the vicinity of the melting point of the solubilizate. These data are plotted in Figure 21 (data—Table VII). A transition point occurred in this system at about 52°C., or 4-6°C. below the macroscopic melting point of *n*-octadecanol. If solubilization takes place at the interface, as the proposed mechanism assumes, an apparent depression of the melting point should be noted. The transition temperature determined here might be considered the melting point of the complex formed at the interface.

As with the nonionic solubilizing agent, a smectic appearance occurred when the solubilizate was contacted with the aqueous solubilizing agent solution or when a suspension at temperatures above the transition point were allowed to cool.

AN ATTEMPT TO DETERMINE SOLUBILIZATION RATES

Because nothing is known regarding the rate at which solubilization takes place, the hope was held, when this study began that some aspects of the kinetics might be explored. Although this phase of the experimental

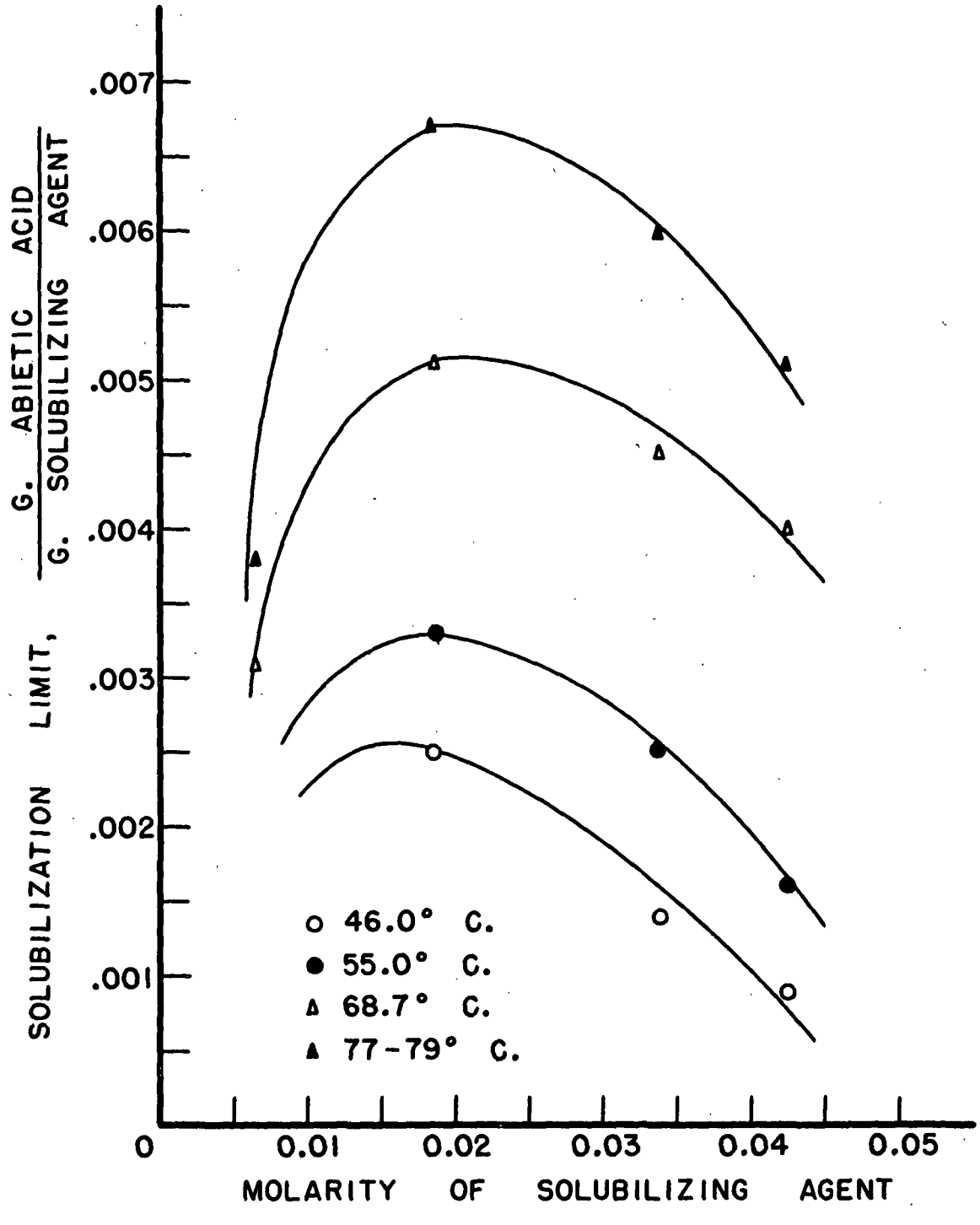


Figure 18. The Solubilization of Solid Abietic Acid by Aqueous Solutions of Sodium Tetradecyl Sulfate

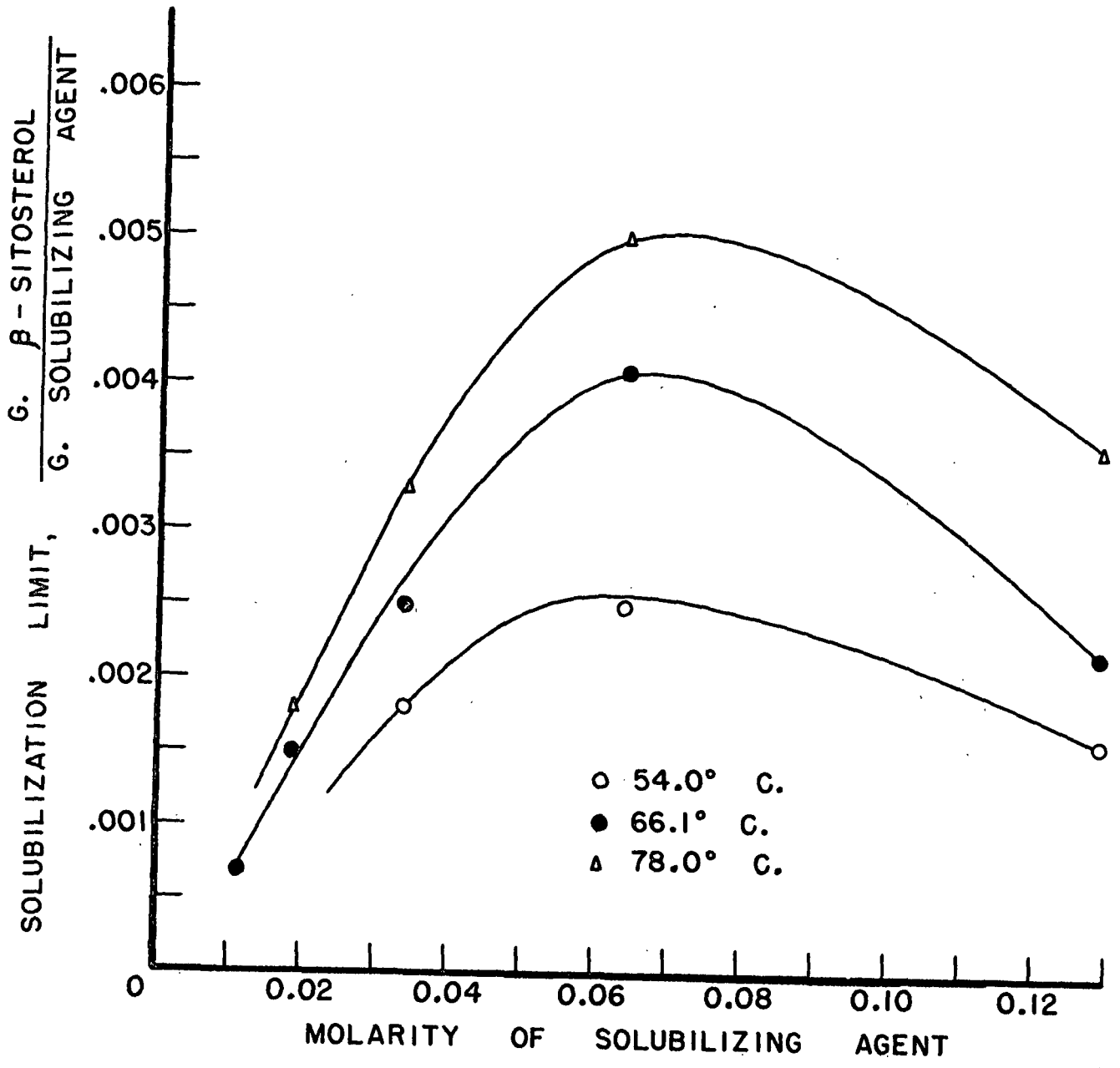


Figure 19. The Solubilization of Solid β-Sitosterol by Aqueous Sodium Tetradecyl Sulfate Solutions

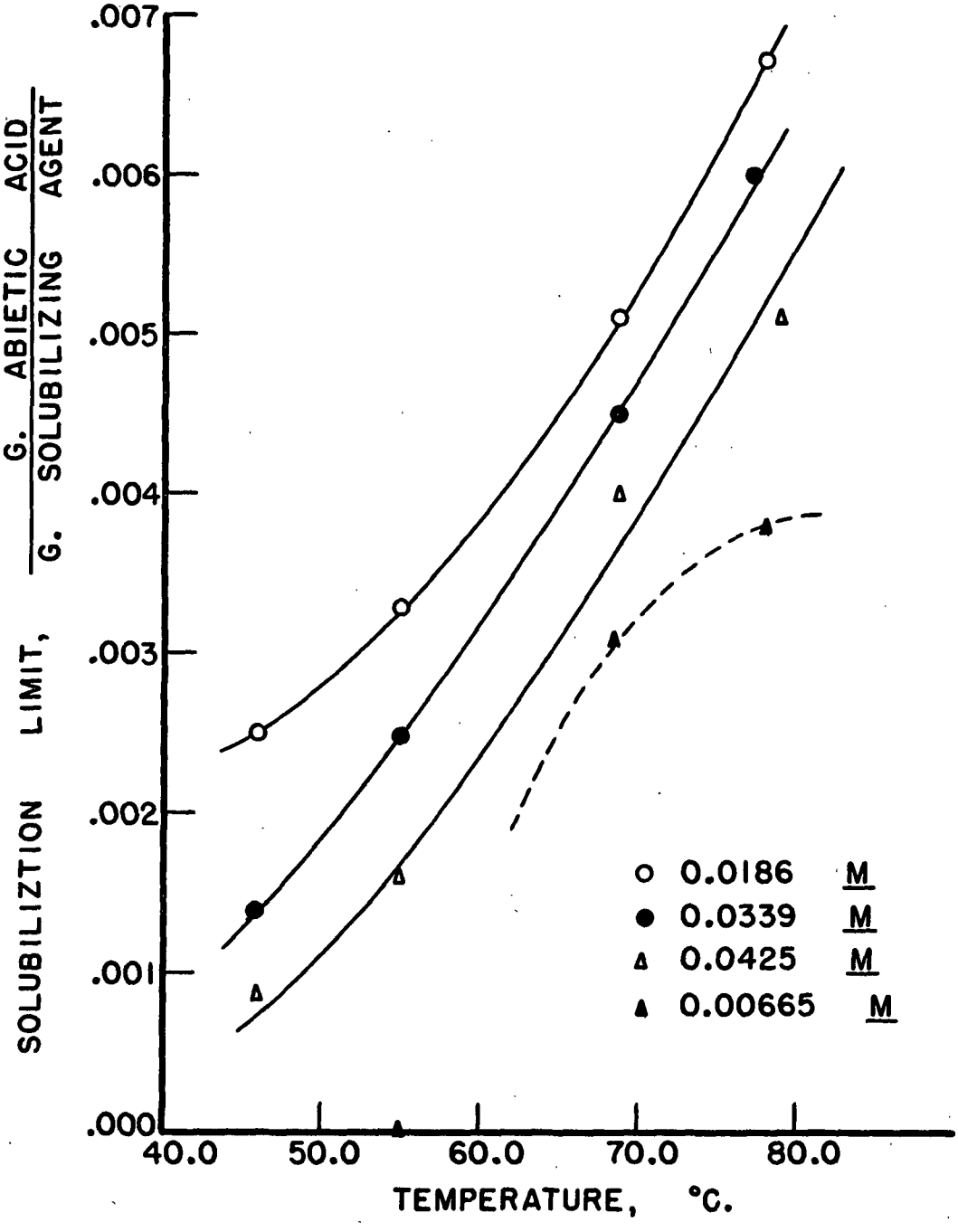


Figure 20. The Solubilization of Solid Abietic Acid in Aqueous Solutions of Sodium Tetradecyl Sulfate

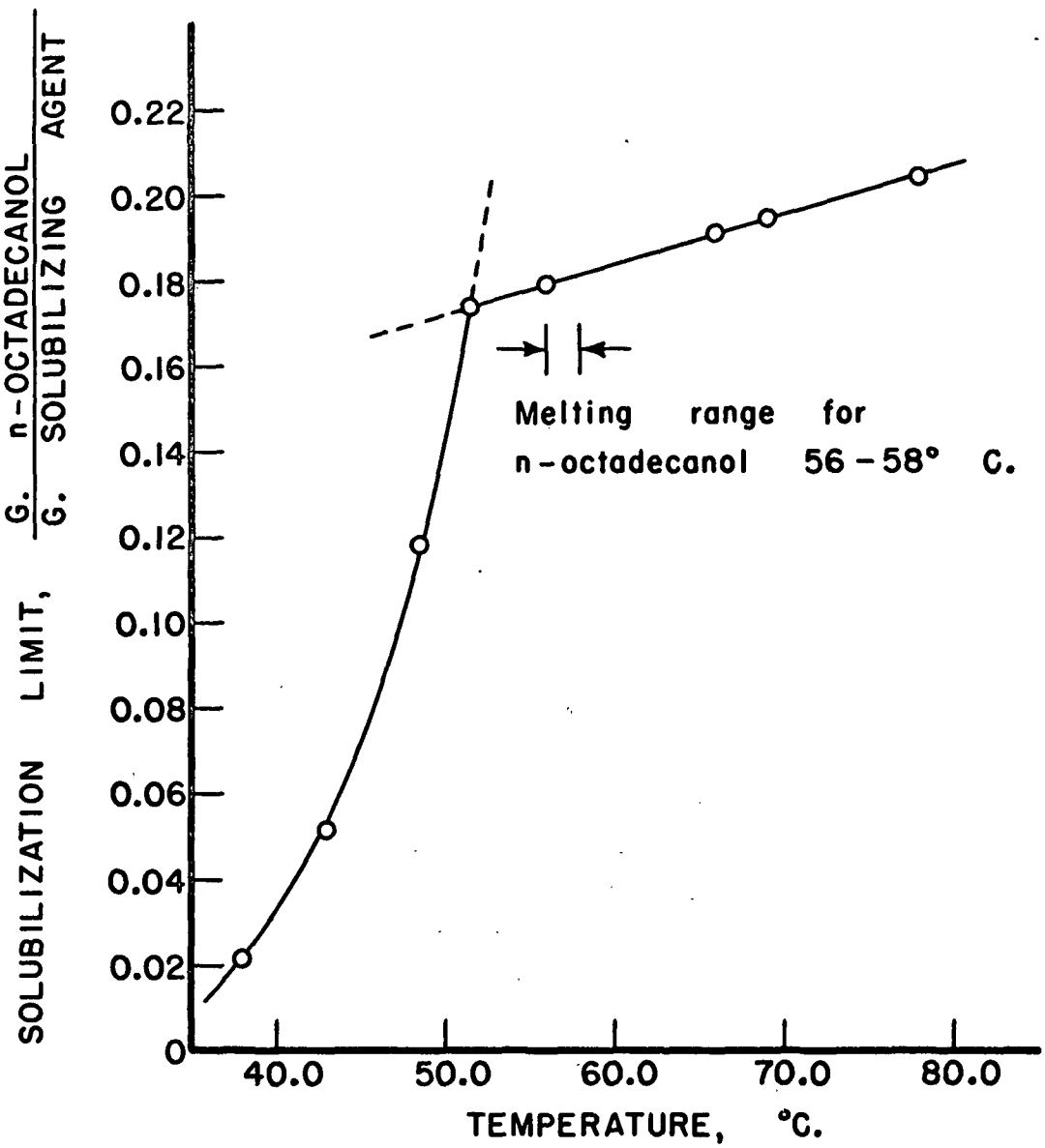


Figure 21. The Effect of Temperature on the Amount of n-Octadecanol Solubilized by 0.121M Sodium Tetradecyl Sulfate

program was later abandoned, a small amount of work of a preliminary nature was conducted.

Here an attempt was made to determine the rate of solubilization of solid n-octadecanol in a 0.121M solution of sodium tetradecyl sulfate using the optical technique which was employed in making the solubilization limit determinations. An emulsion of the n-octadecanol was prepared in water to which a few drops of the solubilizing agent was added, in this case to function as an emulsifying agent. A very finely divided suspension resulted when the ultrasonic generator was used. A small amount (calculated to be less than 75% of the solubilization limit) of this suspension was pipetted into the cell containing 10 cc. of the solubilizing agent solution. The amount of light transmitted by these suspensions was recorded as a function of time. A constant rate of stirring was maintained throughout the experiment. The data obtained from four such experiments are given in Table VIII.

Three experiments were conducted at 38.0°C. At this temperature, coalescence of the individual particles seemed improbable since the particles were solid. An increase in the transmission values for these systems was interpreted as resulting from the disappearance of the dispersed phase. In these three experiments, three different amounts of the suspension were added, corresponding roughly to 25, 50, and 75% of the amount required to reach the solubilization limit. A fourth experiment was conducted at 72.0°C.

The tabulated data indicated that the transmission values of the suspension in the cell increased in a smooth nonlinear manner with time. If the assumption is made that the Lambert-Beer law holds for these systems, the

concentration of the dispersed phase at any time can be shown to be proportional to $\log_{10} 1/T$, where T is the measured transmission value for the system in the cell. When $\log_{10} 1/T$ was plotted against time, curves very similar to those obtained in kinetic experiments illustrating first order reaction kinetics were obtained. This observation suggested a means of rectifying these data. With first order reactions, the experimental data are rectified if the logarithm of the concentration of the reacting substance in a given system is plotted as a function of time. If the data obtained in these experiments do simulate a first order reaction, a (log-log $1/T$) *versus* time plot should rectify this information (i.e., the concentration of solubilizate is proportional to log $1/T$).

In Figure 22, the data have been plotted in the specified manner. The curves numbered 1-3 were obtained from those systems in which the initial concentrations of the solubilizate (*n*-octadecanol) were different, these being 25, 50, 75% of the solubilization limit. If solubilization can be represented, at least mathematically, as a first order reaction, the slopes of the three lines given should be approximately the same. The integrated form of the equation representing a first order reaction is

$$-\log C_A = (k/2.303)\, t + \text{CONSTANT}, \text{ where}$$

C_A is the concentration of the reacting substance in the system at time t, and k is the usual rate constant. The slope of the line obtained from the rectified plot will be equal to $(k/2.303)$. Values of k (reciprocal minutes) of 0.105, 0.102, 0.123 were obtained.

The data obtained at 72.0°C. are plotted in Figure 22 as curve 4. The

TABLE VIII

SOLUBILIZATION RATE DATA

	Time, minutes	T, % Transmission	log 1/T
38.0°C.	1.0	0.747	0.126
	2.0	0.772	0.113
(25% of solubilization	3.0	0.798	0.098
limit added as emul-	4.5	0.831	0.081
sified n-octadecanol)	5.5	0.851	0.070
	6.5	0.867	0.061
	7.5	0.882	0.055
	9.0	0.896	0.047
	10.0	0.908	0.042
	12.0	0.922	0.036
	14.5	0.943	0.025
	17.0	0.955	0.020
38.0°C.	1.0	0.586	0.232
	3.0	0.651	0.186
(50% of solubilization	5.0	0.696	0.157
limit added as emul-	7.0	0.732	0.135
sified n-octadecanol)	9.0	0.763	0.117
	12.5	0.802	0.096
	15.0	0.818	0.087
	20.0	0.843	0.074
	36.0	0.891	0.050
38.0°C.	1.0	0.511	0.291
	2.0	0.522	0.258
(75% of solubilization	3.0	0.586	0.232
limit added as emul-	4.0	0.616	0.210
sified n-octadecanol)	5.0	0.649	0.188
	6.0	0.676	0.170
	7.0	0.701	0.154
	8.0	0.718	0.144
	9.0	0.736	0.133
	10.0	0.753	0.123
	12.0	0.783	0.106
	14.0	0.805	0.094
	16.0	0.826	0.083
	18.0	0.849	0.071
72.0°C.	1.0	0.289	0.673
	2.0	0.439	0.357
(About 10% of solubili-	3.0	0.561	0.251
zation limit added as	4.0	0.680	0.167
emulsified n-octade-	5.0	0.771	0.113
canol)	6.0	0.835	0.078
	7.0	0.878	0.052
	8.0	0.910	0.041
	9.0	0.931	0.031
	10.0	0.935	0.030
	12.0	0.952	0.022

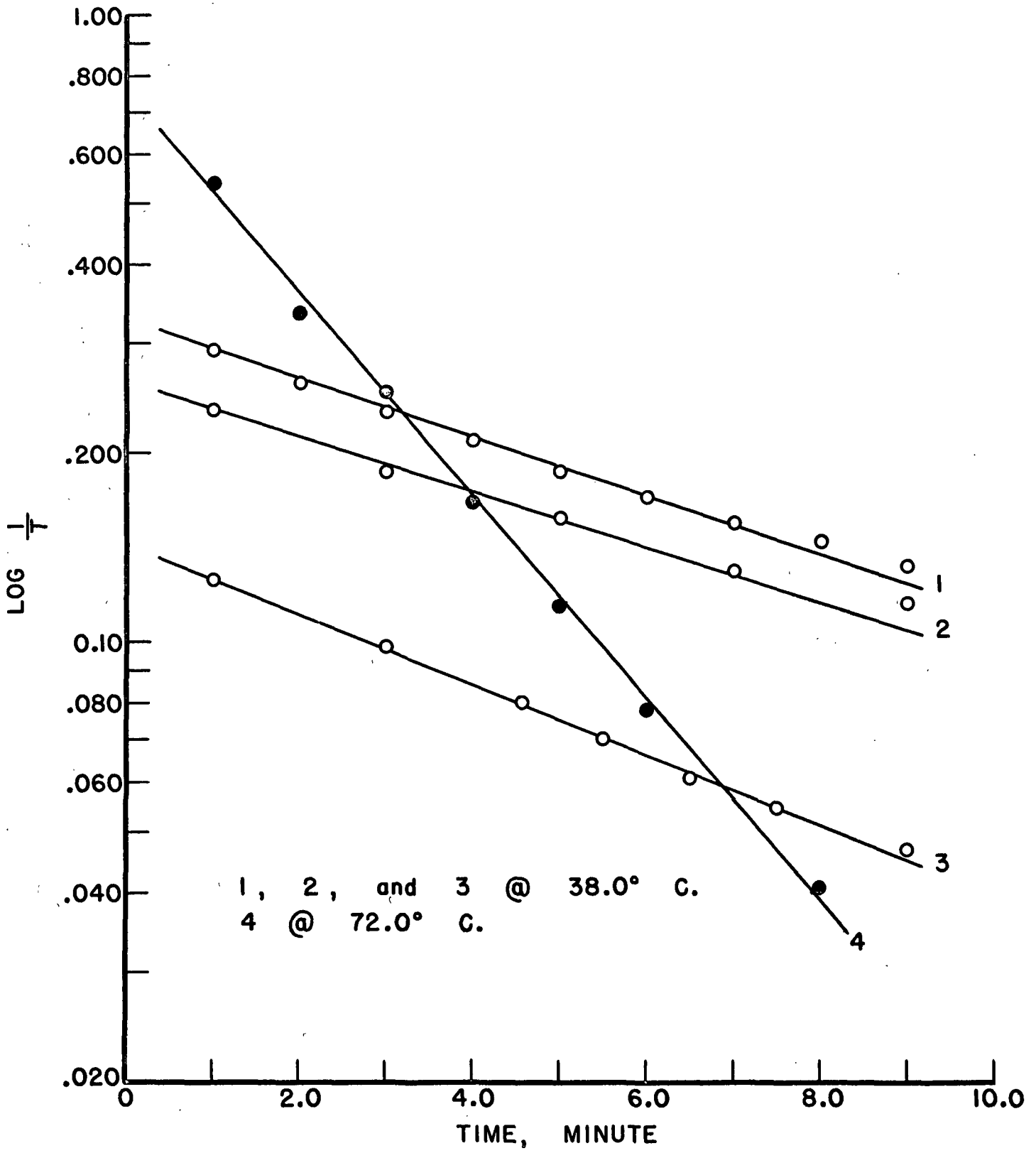


Figure 22. Apparent Solubilization Rates of n-Octadecanol in 0.121M Sodium Tetradecyl Sulfate

apparent rate constant at 72°C. was determined to be 0.383 $min.^{-1}$.

All of the curves plotted tended to level off before all of the solid in the system was fully solubilized, but this was attributed to the presence of relatively large particles in the suspensions, i.e., compared with the bulk of the material.

These results, admittedly meager, do indicate that some information regarding solubilization rates might be obtained in a manner as simple as the one described. The submitted results indicate that solubilization is effected rather rapidly, particularly in systems in which surface effects are minimized by finely dividing the solubilizate.

GENERAL SUMMARY AND CONCLUSIONS

Using a turbidimetric technique, the effects of temperature and the concentration of the solubilizing agent on the solubilization limits of oleic acid and n-octadecanol (in the liquid state) in aqueous solutions of sodium tetradecyl sulfate and polyethenoxy tetradecyl ether (mol. wt. 884) were determined. Temperature effects were explored over a 30°C. range, the maximum temperature employed being about 75°C. The effect of the concentration of the solubilizing agent on the solubilization limit was studied over the relatively dilute range, the upper concentration studied being about 4% for the ionic solubilizing agent and about 2% (by weight) for the nonionic compound.

Regarding the solubilization of both oleic acid and n-octadecanol in the nonionic solubilizing agent, the following observations were made:

1. The quantity of each material solubilized was observed to be dependent upon the concentration of the solubilizing agent solution. When the quantity of material solubilized (moles/liter) was plotted against the molarity of the solubilizing agent solution, a curve slightly concave toward the ordinate was obtained. As the concentration of the solubilizing agent was increased, the slope of the curve tended to become greater, indicating that the efficiency of the solubilizing agent was increasing as the concentration was increased.

2. When these curves were extrapolated to the abscissa, i.e., when no material was solubilized, values near 0.0002M (in the solubilizing agent) were obtained. This concentration, by the usual nomenclature, would be termed the critical concentration. This observation indicates that a certain

minimum concentration is required to insure solubilization, a condition previously known to exist when ionic solubilizing agents were used.

3. Temperature was observed to have no measurable effect on the solubilization of either material, at any concentration level, over the ranges of temperature and concentration explored.

4. An abbreviated set of experiments was conducted to determine the effect of added electrolytes on the extent of the solubilization of these materials at a fixed concentration of the solubilizing agent. Added electrolytes were shown to decrease the quantity of material which a given solution could solubilize, i.e., when compared to that amount which could be solubilized when no electrolyte was present.

Some interesting variations were observed when the same materials were solubilized in aqueous solutions of sodium tetradecyl sulfate, these being:

1. The amount of material solubilized, at a given temperature was a more complex function of the concentration of the solubilizing agent solution than was observed with the nonionic material. The efficiency of the solubilizing agent (on a molar basis) appeared to reach a maximum value, as indicated by an inflection point in plots of moles solubilized/liter versus molarity, when .006 to .010 moles of material were solubilized per liter of solution. Both solubilizates behaved similarly, although the effect was more pronounced when oleic acid was employed as the solubilizate. This behavior was explained as resulting from solubilizate-cation interactions.

2. Temperature effects were observed in the solubilization of oleic acid and n-octadecanol in the ionic solubilizing agent, elevated temperatures in general tending to increase the quantity of material solubilized.

A mechanism has been proposed for describing the solubilization phenomenon and an attempt has been made to treat this subject in a quantitative manner. In this treatment, solubilization is assumed to result from the formation of a complex at the solubilizate-solubilizing agent solution interface, i.e., when the two materials are initially contacted. When a fixed number, β, of the molecules of the solubilizing agent become associated with a single molecule of the solubilizate, the complex is assumed to become water soluble.

The capacity of a given solution of the solubilizing agent for a given solubilizate can then be determined if the nature of the aggregate distribution function for the solubilizing agent solution is known or can be determined. This is necessary since only aggregates of size equal to or greater than β can, according to the proposed mechanism, be considered effective in solubilization. By assuming that the association which exists in solutions of association colloids can be treated in a manner similar to a reversible polymerization, a size distribution function can be derived in terms of an association constant, $\underline{K}$, and the stoichiometric concentration of the solubilizing agent, $\underline{S}_M$. Having the distribution function, an effective concentration for solubilization can be derived. Using this derived expression for the effective concentration, an expression may be derived for expressing the amount of material solubilized as a function of the concentration of the solubilizing agent:

$$\frac{1}{\beta}\left(\underline{S}_M - \sum_{v=1}^{v=\beta} v n_1 {}^{v}\underline{K}^{v-1}\right) = \underline{R} \text{ , where}$$

S_M = the stoichiometric concentration of the solubilizing agent;

β = the solubilization demand, moles of solubilizing agent per mole of solubilizate;

K = the association constant;

$n_1 = \dfrac{2KS_M + 1 - \sqrt{4KS_M + 1}}{2K^2S_M}$; and

R = moles of solubilizate per liter of solution of concentration, S_M, i.e., the amount of material solubilized.

In evaluating the summation term, v assumes the integral values 1, 2, 3...β.

Lacking independent means of calculating either β or K, the derived expression cannot be used directly for estimating the quantity of material solubilized under a given set of conditions. Using an alternative approach, attempts were made to fit the experimental data with an equation of the derived form. Such equation was observed to fit the data derived from the experiments with the nonionic solubilizing agent. The data obtained from the experiments with the ionic material could be fitted over only the range of the more dilute concentrations.

By using this means of solving the equation presented, values for K and β may be obtained. These constants should be useful in correlating the data obtained from different systems and should enable the solubilization phenomenon to be treated in a manner more quantitative than that which heretofore has been possible. The derived constants, for example, enable the effect of temperature on the solubilization limit of the two solubilizates in the ionic agent to be explained quite satisfactorily. The values of the association constant, K, decreased with increasing temperature, the correlation between the association constant and the absolute temperature appearing in

the usual form, i.e., log $\underline{K}=\underline{A}/\underline{T}+\underline{B}$, where $\underline{A}$ and $\underline{B}$ are constants. This observation indicates that the extent of the aggregation is reduced as the temperature is increased. The solubilization demand, β, decreased as the temperature increased, indicating that the solubilizing agent was actually more efficient at elevated temperatures, possibly because the hydrophilic grouping is more highly hydrated under these conditions.

The success of the quantitative treatment employed lends some measure of experimental support to a theory regarding aggregate formation in aqueous solutions of association colloids which differs considerably from the classical approach. In treating the association of this class of compounds, the assumption is usually made that a single preferred aggregate exists in solution when the critical concentration is exceeded. The solubilization data obtained in this work do not support this concept. In order to explain these data satisfactorily, the aqueous solution must be considered to contain a distribution of aggregate sizes (in this work the "most probable distribution" has been used). Actually the distribution function used in this work is based on the mass law. The activity coefficients in all cases have been assumed to be unity. Since dilute solutions have been used, this assumption is probably reasonable. The results obtained in this work indicate that the aggregation process cannot be treated in terms of the existence of an aggregate of fixed size, but rather in terms of a distribution of aggregate sizes.

Abietic acid, n-octadecanol and stearic acid were solubilized from the solid state by aqueous solutions of polyethenoxy tetradecyl ether. The

relationship between the amount of material solubilized and temperature (below the melting point) was observed to be of the same form as that used to correlate data in the case of ordinary solubility determinations, i.e., $\log x_2 = C/T+D$, where x_2 is the mole fraction of solubilizate; T is the absolute temperature; and C and D are constants. Apparently the constant C in this equation, in the case of stearic acid, was related to the latent heat of fusion of this compound.

Neither β-sitosterol nor trimyristin could be solubilized by dilute solutions of the polyether. When small quantities of these materials were first dissolved in oleic acid, however, they were apparently solubilized. This mixture effect was not investigated further.

Only very small quantities of β-sitosterol and abietic acid could be solubilized by aqueous solutions of sodium tetradecyl sulfate at temperatures below the melting points of these compounds. Appreciable amounts of n-octadecanol could be solubilized at temperatures below the melting points of this material.

Regarding the solubilization of solids, the general observation was made that higher temperatures favor solubilization.

PRACTICAL IMPLICATIONS

The importance of solubilization, as originally defined, as a means of dispersing the water-insoluble organic materials commonly encountered in ordinary cleaning operations has never been fully understood. The information obtained from the present study indicates that solubilization might be considered important in some instances, depending on the criterion established for evaluating the role of solubilization in a specific situation. The quantities of oleic acid and liquid stearyl alcohol solubilized in this study by relatively dilute solutions of typical solubilizing agents indicate that three to five parts (by weight) of the solubilizing agent are required to solubilize a single part of solubilizate, assuming that the temperature and concentration variables are established at the proper levels. Individual circumstances would probably determine whether or not solubilization, as such, is to be considered important.

In considering any system composed of detergent-water-fatty organic substance, however, solubilization is inherently involved under equilibrium conditions if the equilibrium diagram presented as Figure 1 may be assumed typical. When the solubilization limit is exceeded, a second isotropic phase is formed as excess fatty substance is added to the system. This second phase may be considered to be a complex formed from three (or more) components of the system. In the present work, the phase formed when excess solubilizate was added to the system was observed to be gelatinous in nature and very easily dispersed. This second phase is assumed to be in equilibrium with the solubilized phase, some solubilized material being present even

though the solubilization limit is exceeded. The important factor to be considered is that the detergent, if present in excess of a certain minimum concentration, is capable of forming a complex with the fatty material, the properties of the fatty substance being destroyed or altered by the formation of the complex.

The question might be raised as to whether a fatty substance must actually be put into homogeneous suspension (i.e., solubilized) to be removed from a substrate. If the energy is supplied to disperse the complex formed when the solubilization limit is exceeded, the fatty material might still be removed from the substrate and suspended. From a practical point of view, the over-all interactions of the components of a given system should be considered, rather than directing attention to a particular region of the equilibrium diagram.

Certain difficulties might be experienced in the two-phase region of the equilibrium diagram. The system is heterogeneous in this region and the possibility exists that the gel-phase might be retained by the substrate either mechanically or by adsorption.

Some general remarks might be made regarding the practical values of the information obtained from the present study which would be of interest in practical pulping operations.

The observation has been made that a certain minimum concentration of the solubilizing agent is necessary for the complex to be formed between the detergent and the fatty material. This observation has been made by other

investigators, but is worthy of further consideration. In the washing of kraft pulp, for example, a high ratio of wash water to pulp could destroy the complex formed between the unsaponified materials of the resin fraction and the resin and fatty acid soaps, causing the unsaponifiables to be thrown out of suspension. These materials might be retained by the fiber, altering the surface properties and the subsequent reactivity of the fiber surface. The observation has also been made that a given compound does not complex with the solubilizing agent to the same extent below the melting point as above the melting temperature. As the pulp and liquor from the digester are cooled, e.g., in the blow tank, free unsaponifiable material might leave the suspension and be retained by the fiber, with the same result as that just mentioned. The same observations might be made regarding the washing stage following the alkaline extraction stage of the bleaching sequence.

In the deresinification of pulps using a detergent in the presence of alkali, the added detergent might function in a number of ways. With alkali alone, saponification of the resin and fatty acids must take place heterogeneously. Once saponified, the acidic materials become soluble and enter the aqueous phase. These materials are solubilizing agents and should be capable of forming a complex with the unsaponifiables present as well as with the fatty and resin acids, providing the over-all concentration of these soaps in solution exceeds the minimum concentration necessary for complex formation. Depending on the consistency and the quantity of the saponifiables present, this minimum concentration may or may not be attained during the alkaline extraction. When a detergent is added, this critical or minimum concentration is produced artificially, the added detergent augmenting

that formed through the saponification of the acidic materials present. Complex formation might be "induced" in this manner and the unsaponifiables removed.

In the deresinification of pulps using detergents, the actual concentration of detergent in the system is of utmost importance, rather than the amount based on the resin content of the pulp or on the pulp. For example, consider an experiment in which sodium tetradecyl sulfate is to be investigated as a deresinating agent in the alkaline extraction stage at temperatures approaching 80°C. If the pulp consistency is assumed to be 10%, 1% sodium tetradecyl sulfate (based on the pulp) must be added to reach the minimum concentration necessary to complex either oleic acid or stearyl alcohol, compounds of the types found in the resin fraction of wood pulps. For efficient deresination, three to four times the minimum concentration should be present in the system. If 1% of the nonionic used in this work is added, under the same conditions, an effective concentration would be present in the system even when the pulp is diluted to a consistency of about 1.5%. This illustration is given because some investigators in the past have overlooked this consideration in using detergents in pulp deresinification. The reported effectiveness of the nonionic products based on ethylene oxide in pulp deresinification may be in part due to the low minimum concentration necessary for complex formation. [In the work presented, the minimum concentration of the ionic agent necessary for complexing oleic acid and stearyl alcohol was higher by an order of magnitude than that of the nonionic for the same compounds, the necessary concentrations being about 0.2% (by weight) for the ionic agent and about 0.02% for the nonionic.]

The added detergent, when present in concentrations above the minimum concentration for complex formation, might actually increase the rate of resin removal. When alkali alone is used, the resin and fatty acids would be saponified at the surface. The reactive surface must also contain molecules of the unsaponifiables in the resin. If the rate of complex formation is rapid enough, the resin and fatty acids might be complexed and removed from the reactive surface, along with the unsaponifiables, before the former are actually saponified. Kinetically, the net reactive surface would be increased in this manner and the rate apparently increased.

The possibility exists that a solubilizing agent might be added to the digester to accomplish some deresinification during the cooking process, particularly in sulfite pulping. A nonionic of the type used in this study containing a high ratio of ethylene oxide to the fatty base would be thermally stable at cooking temperatures. A polyether in the reducing environment, which exists in the sulfite digester, should be chemically stable. Such a treatment might markedly reduce the pitch difficulties commonly encountered with sulfite pulps.

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APPENDIX I

INFORMATION REGARDING THE SYNTHESES AND STABILITY OF THE NONIONIC SOLUBILIZING AGENT

REPRODUCIBILITY OF SYNTHESES

Before beginning a detailed study of the solubilizing properties of aqueous solutions of the nonionic agents, an exploratory study was conducted for the purpose of determining the reproducibility of the polymerization reaction in this laboratory. This was deemed necessary since the reaction is heterogeneous, the possibility existing that variations, batch to batch, might exist.

A total of five condensations were made using n-octadecanol as the fatty alcohol base. In four of these, the weight ratio of ethylene oxide to fatty alcohol was purposely varied. A fifth product was prepared to duplicate one of the four previously prepared products. The study was conducted in this manner so that some small amount of information might be obtained regarding the influence of the ratio of ethylene oxide to fatty alcohol on the solubilizing properties of these solutions.

A purely arbitrary technique was used for evaluating the nonionic solubilizing agents prepared. The amount of oleic acid which could be solubilized by fixed volumes of 3.00% (by weight) solutions of each of these materials was determined at 45.0°C. The results are given in the following table.

Condensate	Weight Ratio: ethylene oxide / n-octadecanol	Amount Solubilized: g. oleic acid / g. polyether	Amount Solubilized: moles oleic acid / mole polyether
1	2.39	0.150	0.515
2	2.59	0.165	0.565
3	2.93	0.170	0.639
4	3.00	0.170	0.643
5	3.00	0.170	0.643

The data indicated that the condensation reaction can apparently be conducted in a reproducible manner. Little more can be deduced from these experiments because the experiments were conducted at a fixed concentration on a mass basis rather than at a fixed molarity as should have been done.

STABILITY OF AQUEOUS SOLUTIONS OF POLYETHERS

When the first attempts were made to conduct solubilization measurements over the temperature range extending from 60-80°C. the results became very erratic for no apparent reason. Duplicate determinations, particularly at 80°C., could not be made.

The first information obtained regarding the reason or reasons for this unusual behavior was gained by examining the aluminum foil used to line the caps of the bottles in which the suspensions were originally prepared. The foil in many cases was discolored and etched. Those liners which had been used in the high temperature determinations were noticeably discolored. When a blank solution (i.e., containing no solubilizate) was placed in the

bath at 80°C., the discoloration of the foil was again noted, but something more unusual was observed. After an hour in the bath at 80°C., the solution assumed a cloudy appearance. After 3 hours, a voluminous precipitate had formed and settled from the solution. On cooling, this precipitate was not totally redissolved. A pH measurement on the suspension, after heating, indicated that the solution was strongly acidic. The information obtained seemingly indicated that the nonionic solubilizing agent in the aqueous solution was decomposing.

Since these materials are polyethers, the most logical first step in ascertaining the nature of the observed decomposition seemed to be to associate the behavior of these polymeric ethers with that of the low molecular weight ethers. Ethyl ether, for example, will absorb oxygen with the resulting formation of a hydroperoxide. This hydroperoxide is believed to decompose giving hydrogen peroxide and ethyl vinyl ether. A literature investigation indicated that little is actually known regarding the formation and decomposition of the hydroperoxides. In almost all instances, however, hydrogen peroxide was determined to be one of the final reaction products.

Quantitative tests for hydrogen peroxide were conducted on the blank polyether solutions which had been heated at 80°C. Positive tests were obtained. Aqueous stock solutions of the polyethers which had been allowed to stand for two to three weeks in stoppered vessels at room temperature also gave weak positive tests. Several commercial polyethers known to contain a high weight ratio of ethylene oxide to fatty alcohol were tested. All except one particular company's product gave positive peroxide tests.

The failure of this one group of materials, very similar to the others, to give a positive test for hydrogen peroxide tended to indicate that these products had been stabilized. A response to a query directed to the company manufacturing the stable nonionics confirmed this suspicion. This company was aware that some oxidizing agent was formed in unstabilized aqueous solutions of nonionics containing a high weight ratio of ethylene oxide to fatty alcohol. Infrared analyses (by the manufacturer) of the decomposition products indicated the presence of carbonyl and carboxyl groups in these materials. A number of common antioxidants were recommended to delay the decomposition.

To utilize the nonionics prepared in the laboratory as solubilizing agents, some means of stabilizing solutions of these materials must be employed. A limited investigation of the effectiveness of a number of the recommended antioxidants was undertaken. In this study, a nonionic containing a weight ratio of 3 parts ethylene oxide to 1 part n-octadecanol was selected as the material to be stabilized. A 3% solution of this material was used in all stabilization experiments. All experiments were donducted at 80.0°C. The apparent stability of the solutions was determined by measuring the pH, this particular property having been observed to decrease rapidly as the decomposition progressed. This means of following the decomposition seemed satisfactory since dilute solutions of hydrogen peroxide are weakly acidic and also because other acidic products undoubtedly result from the decomposition reactions.

A butylated hydroxyanisole, supplied by the Universal Oil Products Company, Chicago, Illinois, functioned satisfactorily as a stabilizer when

1% of this material, based on the nonionic present, was used. Diphenylamine was not effective when used in 1 and 2% amounts. NaI, KI, and $NaSO_3$ also were found to be effective stabilizers. NaI was found to be as effective as any of the investigated materials when 2% of this compound (based on the polyether) was added to the system. The extent to which the solution could be stabilized by the addition of NaI to the system may be seen in Figure 23.

Subsequent solubilization experiments indicated that the added NaI eliminated the difficulties previously encountered at elevated temperatures. At lower temperatures, using oleic acid as the solubilizate, attempts were made to determine the effect of the added NaI on the solubilization limit. The solubilization limits determined for the systems containing NaI were lower by 1-1.5% than the limits determined for the unstabilized solutions.

NaI appeared to satisfactorily fill the requirements of an inert (with respect to the solubilizing properties of these solutions) stabilizing agent and the decision was made to employ this means of stabilization in this work. In the experiments reported in the body of this thesis using polyethenoxy tetradecyl ether solutions, all solutions were made 0.002N in NaI. This concentration of NaI supplied the necessary 2% level for the highest concentration of solubilizing agent used. Comparisons of the solubilization limits for the blank and the stabilized solutions, using both n-octadecanol and oleic acid as solubilizates indicated, as before, that the presence of the NaI in the system depressed the solubilization limit of the stabilized solutions by 1.5%. No attempt was made to correct the measured limits for this effect since the amount of stabilizer in all systems was fixed.

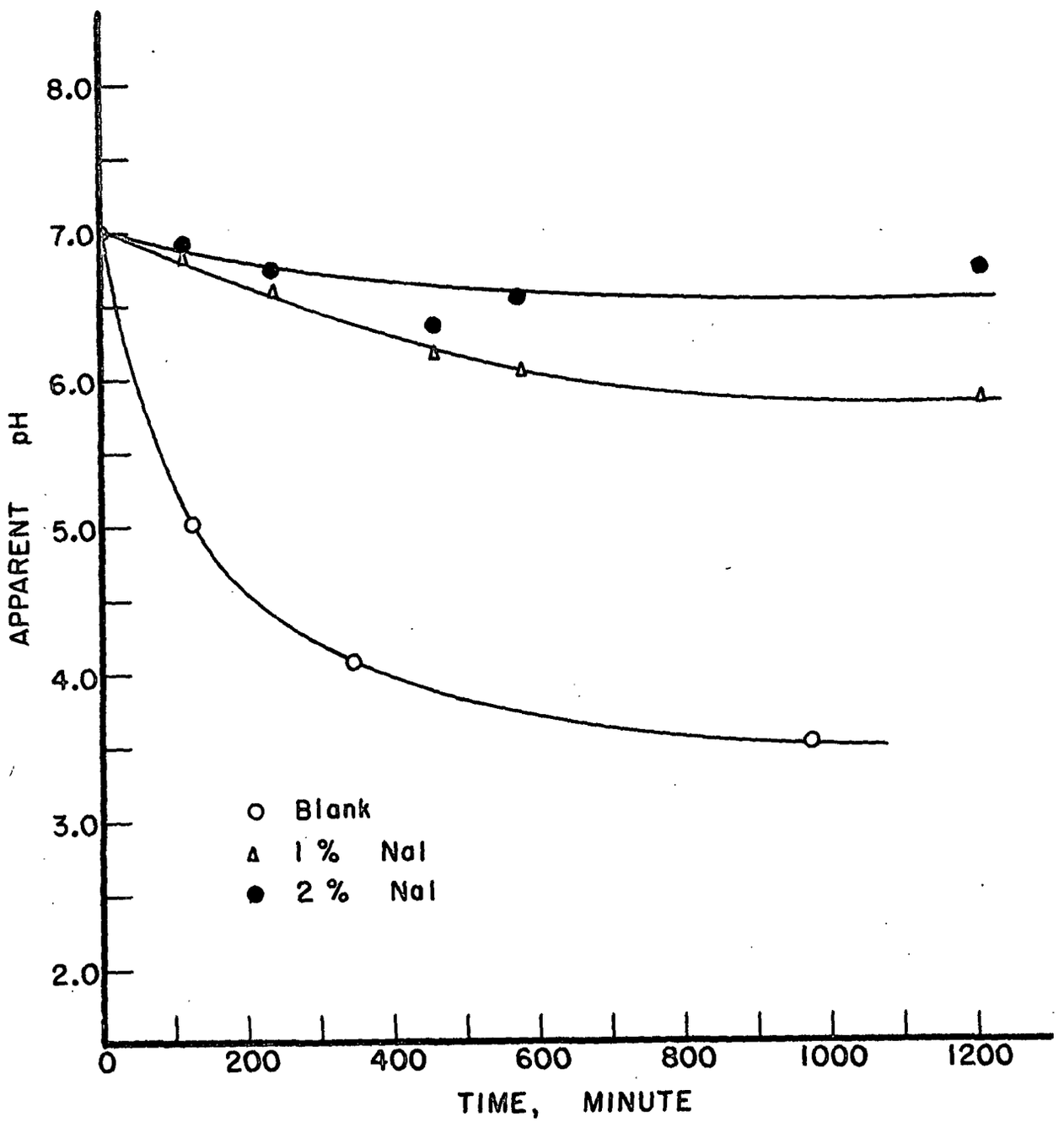

Figure 23. The Stabilization of Aqueous Solutions of Polyethenoxy Octadecyl Ether with NaI at 80.0°C.

APPENDIX II

THE SOLUBILIZATION OF n-DECANOL BY AQUEOUS SOLUTIONS OF SODIUM TETRADECYL SULFATE

Passinen and Ekwall (53) have determined the solubilization limits for n-decanol in aqueous sodium tetradecyl sulfate solutions at 40.0°C. The data obtained from this study are given in Table IX and plotted in Figure 24.

TABLE IX

Molality	Amount n-Decanol Solubilized	
	$\frac{\text{ml.}}{\text{1000 g. soln.}}$	$\frac{\text{moles}}{\text{liter soln.}}$
0.00999	0.65	0.0034
0.0300	2.5	0.0131
0.0700	5.7	0.0299
0.0902	7.1	0.0373
0.109	8.2	0.0430
0.130	10.4	0.0545
0.150	11.3	0.0619
0.170	13.6	0.0715

The observation has been made in the body of this thesis that the aggregation or equilibrium constant K is independent of the solubilizate. From these data (in which sodium tetradecyl sulfate was used as the solubilizing agent) a value of K at 40.0°C. may be obtained. The value of K derived from this set of data has been used in extending the data obtained in the main body of this work in which values of K are related to

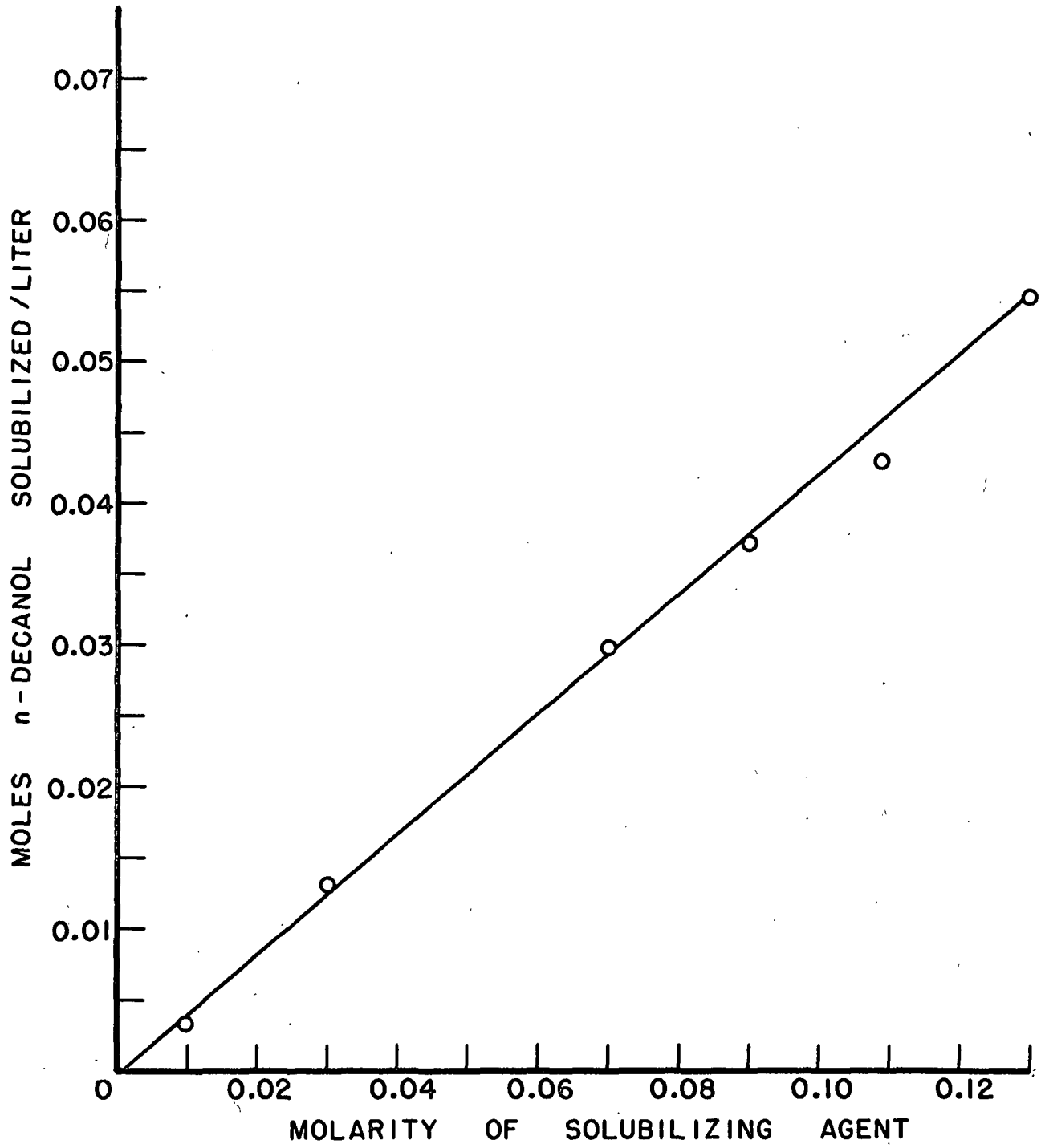

Figure 24. The Solubilization of n-Decanol by Aqueous Solutions of Sodium Tetradecyl Sulfate at 40.0°C. (53)

temperature (Figure 15). Since no determinations were conducted with liquid solubilizates at temperatures of 40.0°C., this set of data enabled a more or less independent observation to be made of the consistency of the quantitative treatment employed.

The original investigators have reported the concentrations of the solubilizing agent solutions used in terms of molarities. In making the calculation of the association constant, the assumption has been made that the two concentration designations are equivalent over the dilute range.

A value for $\underline{K}$ of approximately 6500 was obtained from these data.

APPENDIX III

SAMPLE CALCULATION OF K AND β

To illustrate the manner in which the reported β and K terms were calculated, the data obtained from the series of experiments in which n-octadecanol was solubilized in polyether solutions will be utilized (Figure 7).

To select the proper equation (7-10), an estimate must be made of β. This may be done either by observing or plotting the moles of solubilizing agent necessary to solubilize a mole of solubilizate as a function of the molarity of the solubilizing agent. The values determined for the data under examination are:

Molarity of Solubilizing Agent	Moles Solubilizing Agent / Mole Solubilizate
0.00152	2.00
0.00494	1.88
0.00916	1.77
0.0215	1.64

From this tabulation, β may be estimated as being greater than 1 but less than 2. Based on this estimate, Equation (7) will be used in calculating the association constant, K. The correctness of this estimate can be determined after solving for K.

Corresponding values for S_M and R are then substituted into Equation (7). For illustrative purposes, the following points will be used:

$$\underline{S}_M = 0.0020 \; ; \quad \underline{R} = 0.00095$$

$$\underline{S}_M = 0.0060 \; ; \quad \underline{R} = 0.00325.$$

Upon substitution into Equation (7) two equations in $\underline{K}$ and β are obtained which may be solved simultaneously:

$$0.00200 - \frac{1}{\underline{K}} + \frac{250}{\underline{K}^2}\left(\sqrt{0.008\underline{K} + 1} - 1\right) = 0.00095\beta \qquad (1)$$

$$0.00600 - \frac{1}{\underline{K}} + \frac{83.3}{\underline{K}^2}\left(\sqrt{0.024\underline{K} + 1} - 1\right) = 0.00325\beta. \qquad (2)$$

β may be eliminated by multiplying (1) by (-3.42) and adding (2) to give:

$$0.00084 = \frac{2.42}{\underline{K}} + \frac{83.3}{\underline{K}^2}\left(\sqrt{0.024K + 1} - 1\right) - \frac{855}{\underline{K}^2}\left(\sqrt{0.008K + 1} - 1\right).$$

This equation may then be solved by trial and error for $\underline{K}$. When a value of $\underline{K} = 1400$ is substituted, the equation becomes:

$$0.00084 = 0.00173 + 0.00021 - 0.00111$$

$$0.00084 = 0.00083.$$

By repeating this procedure with different sets of values, the estimate of $\underline{K}$ can be improved. Ordinarily 3 or 4 different sets of values have been used in determining a value for $\underline{K}$. Once satisfied with a value for $\underline{K}$, a value for β may be determined by substituting the derived $\underline{K}$ value and solving for β.

Under some circumstances, linear approximations to Equations (7-10) may be made. In the present case, this procedure is <u>not</u> appropriate but for illustrative purposes will be considered. When the conditions permit, Equation (7) may be simplified to give:

$$\frac{1}{\beta}\left(\underline{S}_M - \frac{1}{\underline{K}}\right) = \underline{R}.$$

In this case, the constants may readily be evaluated from the slope and intercept, i.e., a straight line will reasonably fit the data plotted in Figure 7.